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A STUDY OF THE DEPOSITION OF CARBIDE
COATINGS ON GRAPHITE FIBERS

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FINAL REPORT

A STUDY OF THE DEPOSITION OF CARBIDE
COATINGS ON GRAPHITE FIBERS

By

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FOREWORD

The work described herein was done at the Avco
Specialty Materials Division under NASA Contract
NAS1-15374 with Mr. Dennis L. Dicus, NASA Langley
Research Center, as technical representative of the contracting
officer.

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ABSTRACT

The chemical vapor deposition of boron carbide and silicon carbide on graphite fibers to increase their electrical resistance was studied. Silicon carbide coatings were applied without degradation of the mechanical properties of the filaments. These coatings typically added 1000 ohms to the resistance of a filament as measured between two mercury pools. When SiC-coated filaments were oxidized by refluxing in boiling phosphoric acid, average resistance increased by an additional 1000 ohms; in addition resistance increases as high as 150 K ohms and breakdown voltages as high as 17 volts were noted. Data on boron carbide coatings indicated that such coatings would not be effective in increasing resistance, and would degrade the mechanical properties.

SUMMARY

The accidental release of graphite fibers from composites may pose a hazard to electrical equipment. In this work, the chemical vapor deposition of high resistance coatings was investigated. Deposition conditions were found which produced SiC coatings of thickness on the order of several tenths of a μm without degrading the underlying filament. SiC-coated graphite filaments were also oxidized under conditions which did not degrade their strengths by refluxing in boiling phosphoric acid. The current-voltage curves of the coated and coated-oxidized filaments were non-linear. An empirical resistance measurement showed that the SiC coating added 1000 ohms to the resistance of a filament when measured between one cm deep mercury pools. After oxidation, the resistance was increased by up to 150,000 ohms and breakdown voltages of up to 17 volts were observed. Oxidation increased average resistance by an additional 1000 ohms. Further work is required to increase the uniformity of the oxidation procedure.

Electrical measurements of B_4C coatings on carbon monofilament showed that thin coatings would be ineffective in enhancing electrical resistance. The deposition of boron carbide onto graphite filaments seriously degraded their strengths.

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INTRODUCTION

The increasing use of graphite--organic matrix composites in aerospace applications and projected large volume utilization in commercial aviation has led to a concern about possible problems arising from the accidental release of the filaments, say in a fire environment. The low density of the filaments along with their small diameters (ca. 6-8 μm) leads to a small atmospheric settling rate and hence to the possibility of wide dispersal. Under these conditions the high electrical conductivity of the filaments could, it was feared, lead to malfunction of electrical equipment.

A multifaceted program was initiated by NASA to assess possible risks and to diminish those risks through various strategies. Reference 1 outlines the scope of the program. One of the approaches taken towards diminishing possible risks is the coating of the filaments with materials with high electrical resistivity. The insulating coatings would decrease the likelihood of adverse effects in the case of their accidental release. This contract is part of that coatings effort.

Ideally, such coatings should have the following effects on the filaments:

1. They should substantially reduce their electrical conductivity.
2. Overall density should not be appreciably increased.
3. Mechanical properties should not be adversely affected.

In addition, composite properties using coated filaments should be comparable to those made from uncoated filaments.

Given these general goals, the specific goals of this program were to coat the graphite filaments in a yarn with 0.1 μm thick layers of SiC and B_4C . These layers were to be deposited by chemical vapor deposition under conditions where the mechanical properties of the filaments are not adversely affected. Further, SiC coated filaments were to be oxidized to convert the SiC to SiO_2 . Finally, the electric and dielectric properties of the coated filaments were to be determined. The graphite used in this work was Thornel 300.

During the course of the work, it became apparent that the application of B_4C coatings was not technically feasible within the scope of the contract. Program objectives were achieved with respect to the SiC and SiO_2 coatings, however.

Although not primary goals of this work, the coatings produced offer possible advantages in other applications of graphite by enhancing the thermo-oxidative stability of polyimide matrix composites and by improving filament matrix bonding in metal-matrix composites.

I. Chemical Vapor Deposition Coating Reactor

A. Vertical Reactor

The initial reactor and filament handling system is illustrated in Figure 1. In operation, graphite yarn is pulled off a supply reel under the controlled tension, passes over a tachometer and enters the reactor through a mercury seal. While in the reactor, the filament is resistively heated in the plating gas mixture. Electrical contact is made through the mercury gas seals. The power source is 110V AC controlled by a variable transformer. Upon emerging from the reactor through the bottom mercury seal, the yarn is collected by a variable speed traversing take-up spool drive.

The reactor is shown in detail in Figure 2. The two upper gas inlets are connected to metered gas supplies; different mixtures of silanes, hydrogen, nitrogen, argon, propane and air in arbitrary proportions can be admitted to the reactor at both inlets. The bottom inlet is connected to hydrogen, argon and propane. The exhaust stream is connected to a system which condenses, distills and recycles the silanes.

A critical design feature of this reactor is the geometry of the entrance and exit slits in the mercury gas seals. The slits must be small enough so that mercury is retained by its own surface tension and yet large enough to permit free passage of the graphite yarn. This could in fact be achieved for brief periods of operation. However, loose graphite filaments and snarls in the as-received graphite tended to collect in the slits, causing a jam-up after several minutes of running. To alleviate this difficulty, a horizontal reactor design was adopted.

B. Horizontal Reactor

The horizontal reactor is shown in Figure 3. The yarn enters and exits the reactor through shallow U-tubes filled with mercury. Near each mercury seal is a gas inlet for hydrogen and argon. The major purpose of these gas flows is to control local hot spots caused by stagnant gases near the ends of the reactor. The hydrogen flow at the inlet side does become mixed with the plating gas and must be included in determining its composition. Also included in this design are protuberances on the inner surface of the reactor near the gas seals which act as yarn spreaders, ensuring more uniform deposition throughout the yarn. The effective length of the deposition zone is controlled by the separation of the main gas inlet and exhaust ports. As in the vertical reactor, a wide range of gas mixtures was available at the inlet.

The reactor used for the bulk of the work in this report had a length of 36.8 cm between gas seals and an effective deposition zone of 15 cm.

II. Qualitative Characterization Procedures

A. Yarn Breaking Loads

For expediency during coating optimization experiments, we required a rapid qualitative test that would at least show up serious filament degradation. We found that tensile testing a dry bundle of filaments, while not yielding data which could be related to the actual tensile properties of the filaments, did give sufficiently reproducible values to be useful as a guide. Samples of yarn were cut to approximately 10 cm; two pieces of 2.5 cm wide masking tape were folded over each end of the length with a 2.5 cm length yarn in between. The samples were held in the pneumatic grips of a tensile testing machine set at a 2.5 cm gauge length, and tested. We found that as-received T-300 gave an average tensile load of 107N with a standard deviation of 12N. Yarn which had been pulled through a cold reactor gave average tensile loads of 102N; hence the mechanical handling of the fibers during the deposition process appeared not to significantly effect the dry bundle strength as determined this way. In addition, heating the fibers in an argon atmosphere to deposition temperatures (1000-1400K) gave average loads of 98N, indicating that any degradation effect from this source was small.

B. Yarn Electrical Resistance

In contrast to the more sophisticated procedures later used to characterize coatings, a quick and simple test was devised to give qualitative indications as to whether a particular coating run had changed the filament properties. Samples of yarn were placed across two parallel copper foil strips 2.5 cm wide and spaced by 2.5 cm. To provide reproducible pressure, the yarn was weighted down on each foil by a copper-foil-covered aluminum block of dimensions 2.5 x 5 x 4 cm. Resistance measurements were taken with an ohm meter across the gap between the foils. As-received yarn gave resistances in the range of 5.5 to 6.5 ohms measured this way.

C. SEM Examination

Particular batches of coated yarn were submitted for SEM examination in order to assess coating texture, uniformity and thickness. Samples were typically coated with a few atomic layers of palladium to eliminate any charging effects due to insulating coatings.

III. Carbide Coating Optimization

A. Plan of Attack

Previous experience with SiC deposition provided a starting point for the plating gas composition. The first areas studied in this program were the strength and electrical resistance of yarns coated at different temperatures in this starting gas mixture. Next, residence time was optimized at temperatures near optimum. Finally, at optimum temperature and residence

time, variations in plating gas composition were studied. These consisted of varying the silane to hydrogen ratio and of studying the effects of dopants, in particular propane and N_2-O_2 mixtures, on the properties.

B. Deposition Temperature

The initial plating gas composition consisted of 0.425 l/min. of an approximately 1:3 mixture of methydichlorosilane and dimethyldichlorosilane and 0.5 l/min. of hydrogen. In addition, 0.3 l/min. of hydrogen was admitted to the reactor at both the entrance and exit ports to prevent stagnation and overheating. The filaments were incandescent only in the region between the reactant gas inlet and the exhaust outlet. In the deposition zone, temperatures were measured with an optical micropyrometer. Residence times of 5 ± 1 second were used in this part of the work. After coating, resistance and strength were measured as described in Section II. In the discussion below, strengths are reported as percent of untreated yarn strength.

The results are shown in Figure 4. In this set of data there is a catastrophic loss of filament strength at deposition temperatures above about 1120K (1560°F). The resistance passes through a maximum as deposition temperature is increased. At a deposition temperature of 1060K (1450°F), the resistance of the "coated" yarn is the same as that measured for untreated material, with a three to fourfold increase at about 1150K. The resistance drops off at higher temperatures.

Figure 5 shows the results of another set of runs with a 4.5 second residence time. In this case the drop-off in strength with increasing temperature is less severe, but the conclusions are the same; the optimum deposition temperature is in the range from 1080-1120K.

Another point to note from the data is the drop-off in resistance with increasing temperature which appears in both sets of data. With equal residence times, the coatings would be thicker at higher temperature; hence the fall in resistance indicates that the electrical resistivity of the deposit decreases with increasing deposition temperature.

C. Residence Time

For the purpose of producing sufficient material for a meaningful test, the object of this portion is to find the shortest residence time consistent with coating quality. Figure 6 shows the results of a set of runs at the standard gas flows and optimized temperature. The data indicate a consistent trend of strength degradation with increasing residence time. Hence, we chose times in the range of 4-6 seconds for experimentation with variations in plating gas composition. Subsequent metallographic analysis showed that this range of time and temperature was producing coatings near the 0.1 μm target thickness.

D. Plating Gas Composition

Previous experience with SiC deposition indicated three aspects of plating gas composition which would be expected to have effects on the coatings: variations in the silane to hydrogen ratio, addition of propane to the plating gas, and doping the filament coating with mixtures of oxygen and nitrogen. These are discussed separately below:

1. Propane Conception

Several sets of experiments were performed to assess the effects of the addition of 0.10 l/min. of propane to the plating gas. The results are presented in Table I. The experiments show a small improvement in strength retention with the addition of propane to the plating gas, while there is no clear effect on the resistance.

The set of data in this table also illustrates that the strength and resistance of yarns coated under similar conditions are only reproducible within broad ranges. The coating conditions for runs 22 and 25 were nominally identical; yet the strengths were approximately 8% different while the resistances were approximately 50% different. The magnitudes of the variations noted above were typical of those observed for these two properties during the study.

2. Dopants in Plating Gas

Experiments were conducted to investigate the possible effects of the addition of a dopant on the electrical properties of the coatings. The material selected was a 1% mixture of oxygen in nitrogen. Table II presents the results of a set of experiments showing the effects of addition of 0.04 l/min. of the oxygen mixture. Runs were performed both with and without propane additions. The results show that when propane is absent, there is no clear trend for either strength or resistance with the addition of the dopant. When propane is present, the dopant increases the yarn resistance, but does so at the expense of strength. It was decided not to add the O_2-N_2 mixture to the plating gas for the production of the deliverable coated material.

3. Variations in Hydrogen to Silane Ratio

As noted above, the standard gas flows chosen as a starting point consist of 0.425 l/min. of silanes and 0.5 l/min. of hydrogen. In addition a flow of 0.3 l/min. of hydrogen injected at the entrance mercury electrode mixes with the plating gas. Approximately twenty runs were made in which the proportion of hydrogen to silane was shifted to either side of the starting point. Variables tested in addition were different deposition temperatures in combination with different gas composition, the addition of propane and O_2-N_2 mixtures, and dilution of the plating gas with argon. The mechanical properties of yarns coated under these various conditions were consistently poor, averaging less than 50% strength retention. Examples of some of these results are shown in Table III.

E. Optimized Conditions

The optimized coating conditions found consisted of a residence time of 5 sec. (drawing rate of 120 cm/min. through a 10 cm reaction zone) at a temperature in the range of 1080 - 1120K. The plating gas consists of 0.425 l/min. of the silanes, 0.1 l/min. of propane and 0.8 l/min. of hydrogen, 0.3 l/min. of which is introduced at the mercury gas seal and electrode. Approximately one kilogram of graphite was coated under these optimized conditions for delivery to NASA.

F. Coating Characterization

In coating high filament count yarns, a primary concern is the uniformity of the coating through the entire yarn. The goal is to have the deposition limited by reaction at the surface rather than gaseous diffusion rates, since the latter would lead to encapsulation of the yarn rather than coatings on individual filaments. Figure 7 shows an SEM of a part of a yarn coated for a residence time of 60 seconds in a static test of the CVD reactor. Gas flows (in l/min.) for silanes, hydrogen and argon were 0.425, 0.8 and 0.05 respectively. Deposition temperature was approximately 1300K. Examination of the whole cross section of the yarn shows a coating of the type illustrated on all the filaments; hence the coatings do permeate the entire yarn. The bridging between filaments seen here is not expected, nor was it observed with thin coatings.

The morphology of the coatings was temperature dependent. Figure 8a illustrates the coating produced at the highest deposition temperature attempted, approximately 1400K. The coating is characteristic of a rapid growth process resulting in large grain deposits. Figure 8b shows the surface of a single filament coated at 1170K. While some irregularities in deposition can be noted at high magnification, the coating is far smoother and only partially masks the texture of the graphite. Figure 8c shows filaments coated at the optimized conditions. The change in texture between coated and uncoated graphite is not dramatic; the presence of a Si peak in the accompanying EDAX scan demonstrates the presence of the coating.

A great deal of difficulty was encountered in attempts to accurately measure coating thickness with the techniques available to us. SEM photomicrographs generally provided insufficient contrast to clearly resolve the coating. The best resolved photo is one obtained from a polished sample by optical metallography. It is shown as Figure 9. Although of insufficient magnification to allow precise thickness measurement, it does show a coating in the range of tenths of μm . The coating in this case was produced under the optimized conditions.

Mechanical and electrical properties of coated and oxidized filaments are discussed below in Section VII.

G. B₄C Coatings

The data in the literature demonstrates that in the chemical vapor deposition of B₄C, there exists a very narrow range of conditions under which the desired material is deposited (Ref. 5). Parallel work at Avco on a proprietary B₄C deposition process licensed from SNPE in France shows the same results. Solid deposits formed from a BCl₃, H₂, CH₄ reaction mixture are typically mixtures of B₄C with either excess carbon or boron unless gas compositions are held within a very narrow range ($\pm 1\%$) of the optimized conditions. Hence the scan of plating gas composition, as was done with SiC deposition, was not done for B₄C deposition.

Further, the deposition "window" is temperature-sensitive. In establishing a production capability for making B₄C coated boron filaments, the plating gas composition had been well defined for a deposition temperature in the neighborhood of 1575K.

Hence, B₄C coating was attempted at the optimized gas composition at the normal deposition temperature. The drawing rate of the yarn through the reactor was the maximum for the reactor as set up. The result was a catastrophic deterioration of the mechanical properties of the yarn with over 90% loss of strength.

As discussed below, parallel measurements were underway on the electrical properties of SiC and B₄C coatings on carbon monofilaments. These measurements indicated that B₄C coatings less than 1 μm thick would be ineffective in increasing fiber electrical resistance.

Even if a substantial effort led to deposition conditions at another temperature which did not degrade the fiber, there was evidence that coating would not produce the desired increased fiber resistance. Therefore, it was decided that within the scope of the present program, it was not technically feasible nor desirable to proceed further with deposition studies of B₄C coatings.

IV. Oxidation of SiC Coatings

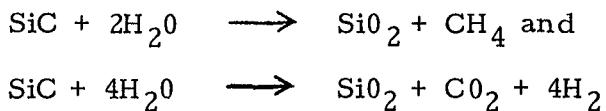
One objective of the program was to oxidize one pound of SiC coated graphite filaments with the aim of converting the SiC to SiO₂. The SiO₂ has a much lower electrical conductivity than SiC; hence resistance of the coated and oxidized filaments should be greater than that of the as-coated filaments.

Silicon carbide itself is widely used for high temperature applications because it is highly oxidation resistant. Data in the literature (Ref. 2) indicates that the rate of oxidation of SiC is enhanced by the presence of water vapor and in fact, proceeds an order of magnitude faster in pure water vapor than in pure oxygen.

Samples of coated tows produced at run conditions in the neighborhood of the optimized conditions were placed in alumina boats in a tube furnace. The atmosphere in the furnace was an argon-water vapor mixture prepared by bubbling argon through water held at 323K (50°C). Runs were conducted at temperatures from 1073K to 1273K (800°C - 1000°C) for times from five minutes to twenty-five minutes. The results are presented in Table IV. The only conditions which produced appreciable changes in resistance also produced appreciable mass loss and severe degradation of filament strength as inferred from yarn breaking loads.

The other known etchants for silicon carbide are molten metals, fused salts and phosphoric acid.

At 488K, silicon carbide reacts, with water in the presence of phosphoric acid via two routes: (Ref. 3).



Under similar conditions, graphite was found to be totally unreactive. (Ref. 4).

We conducted preliminary tests by immersing lengths of SiC coated yarn in refluxing boiling phosphoric acid. Two acid mixtures were tried: 85% acid, boiling at approximately 438K (165°C) and 100% acid, which boils at 488K (215°C).

Filaments were held in the mixtures for one hour. After treatment, they were washed until the pH of the rinse water no longer changed, and then were rinsed with distilled water. Fibers were dried in an air circulating oven held at 368K (95°C).

Neither treatment affected the strength of the filaments as inferred from measurements on the yarns. The resistance of the sample treated at 438K, as measured on the tow increased tenfold to approximately 200 ohms, while the resistance of the fibers treated at 488K (215°C) was virtually unaffected. We can postulate that the enhanced reaction at the lower temperature is due to the higher concentration of the oxidant, water. At 488K (215°C), the only source of water is the decomposition of the phosphoric acid.

One lot of 450 grams of SiC coated filaments were wound on glass spools, each spool holding approximately 50 grams of filaments. The spools were perforated to allow acid solution to permeate the yarn thoroughly from both sides. The spools were immersed in a 3 liter vessel to which could be attached a reflux column. Each spool was held in boiling 85% phosphoric acid at 438K for two hours and then rinsed and dried as previously described. The nine spools were referred to as oxidation batches 1 through 9 and subsequently shipped to NASA as contract deliverable items. Mechanical and electrical properties of these fibers are discussed in Section VII.

V. Electric and Dielectric Properties of SiC and B₄C Coatings on Carbon Monofilament

In parallel with the graphite coating experiments, studies were performed on the electrical properties of coatings applied to 33 μm diameter carbon monofilaments (CMF). In this way, some information on electrical properties could be generated independently of the development of the coating technology.

The apparatus used is shown in Figure 10. The regulated D. C. power supply is continuously variable between 0 and 50 volts; accuracy is at least $\pm .05$ volts in the lower ranges and $\pm .2$ volts at the higher voltages. Current measurements were made with either a 0-2.5 μA or 0-50 μA meter; shunting increased the readable ranges to as high a value required. Alternatively, an ohm meter could be connected across the electrodes. Assuming that the coating acts as a resistor, a model for the circuit equivalent to the coated filament is shown. The high resistivity of the coating materials makes it likely that the conduction occurs primarily in a path through the coating, then along the graphite, and then back through the coating at the other electrode.

The measurement procedure was to place the filament under study in the electrodes and record current levels at a number of voltage levels. The voltage across the load resistor was calculated from the current and the known value of the resistance, giving by difference, the voltage across the filament. The semi-conducting properties of SiC make such a procedure necessary.

Coatings in the thickness range from less than one μm to fifty μm were investigated. Samples of both B₄C and SiC were prepared by the standard Avco CVD process for manufacturing filaments. For the SiC coatings, plating conditions were similar to the optimized conditions found earlier except that deposition temperature was in the range from 1500-1700K.

The non-linear nature of the current voltage curve for a 29 μm thick SiC coating on carbon monofilament (CMF) is shown in Figure 11. The voltage axis represents the voltage seen by the filament after the voltage drops in the load and measuring parts of the circuit have been subtracted from the imposed voltage. At all voltages, there is a significant curvature to the I-V plot; hence, a usual type of resistance measurement would give a value quite sensitive to the probe voltage. In this case, the current became unstable at approximately 3.6 volts. If the system were behaving like a pure semiconductor, the slope of the curve above 30 μA would be negative.

The non-linear I-V behavior was even more apparent for very thin SiC coatings. Figure 12 shows the behavior of a thin SiC coating. (Precise thickness measurement was difficult on this particular sample.) Optical microscopy indicated the presence of a coating less than one μm

thick. At small currents, the filament acts like a resistor, with a resistance in the range observed for the underlying carbon monofilament. A transition point is reached at approximately 1.5 volts and 2.5 ma at which the voltage drop across the filament decreases for increasing current; the system behaves as a semiconductor with a negative impedance of approximately 1000 ohms. Decreasing the current brings the sample back to near the original current-voltage curve. The filament was changed by this; a second attempt showed qualitatively similar behavior, but at different currents and voltages.

Figure 13 and 14 show the I-V characteristics of samples 3.3-4.2 μm and 8.5-9.0 μm respectively. (The range in thickness arises from separate measurements, one with a filar eyepiece and the other with an image splitting eyepiece.) Current-voltage characteristics are non-linear at all voltage levels.

A measure of "resistance" was obtained from the slope of the curve extrapolated to zero current. Note that a resistance measurement made with an ohm-meter would be sensitive to the test voltage, and most likely would give a smaller value, perhaps as much as a factor of 5 smaller. The resistances obtained by extrapolation are plotted vs. thickness in Figure 15. For reference, one may note that the resistances are approximately three orders of magnitude larger than those for B_4C coatings discussed below.

The extrapolations to zero current also provide a measure of breakdown voltage at which conduction begins. For all samples, this was on the order of only several tenths of a volt. This is a combined effect due to two mercury - SiC interfaces, two SiC-CMF interfaces and two paths through the SiC. The experiments did not provide a means for separating these various effects.

Some qualitative tests were performed to assess the effects of oxidizing the SiC to SiO_2 . A number of samples of 55 μm thick SiC-coated CMF were heated for various lengths of time in the strongly oxidizing region of a propane-air flame. Current-voltage curves showing the range of observed behavior are shown in Figure 16. The results show that high breakdown voltages can be achieved through oxidation. Sample No. 24 had a breakdown voltage of 45 volts and exhibited a resistance of 2500 megohms past breakdown. Subsequent SEM examination of this sample showed a diffuse surface layer approximately one μm thick. SIMS examination was inconclusive, but was consistent with this layer being silica.

As previously noted, the electrical properties of SiC coatings were changed after current had been passed through them. The same was true of the oxidized coatings. Figure 17 shows the results of three tests on the same sample of oxidized SiC (55 μm thickness). By the third test, the coating is completely ineffective.

This behavior is consistent with very localized conduction through the coatings, resulting in damaged coatings through local heating.

A similar investigation was performed to study the electrical properties of thin B_4C coatings. Six carbon monofilament samples with coatings ranging from 1.4 to 9.3 μm in thickness were examined. Thicknesses were determined with a filar eyepiece at 1000X using an optical microscope. The general trend observed in the measurements is shown in Figure 18: All samples showed linear volt-ampere characteristics at low voltages, followed by non-linear behavior. As coating thickness increased, the onset of non-linear I-V behavior occurred at higher voltages and became less severe.

Figure 19 shows the current-voltage characteristics at the low voltage end of the measurement range. As noted above, in the range, the curves are all linear, with a slope corresponding the inverse of an ohmic resistance. Extrapolations to zero current lead to stand-off voltages between 0.1 and 0.2 volts. The resistance values obtained from the slopes are plotted in Figure 20. Also shown (as a band on the graph) is the typical resistance measured for the uncoated carbon monofilament substrate. As the graph shows, boron carbide coatings become completely ineffective in enhancing resistance at thicknesses of one μm and below. It is possible that some of the values obtained reflect imperfections (such as holes or cracks in the coatings); however, the extrapolation from larger thicknesses leads to the same conclusion.

VI. Characterization of SiC and Oxidized SiC Coatings on Graphite

A. Mechanical Properties

Individual filament mechanical properties were measured for as-received, SiC-coated and oxidized filaments. The filaments were mounted on cardboard frames with fast-curing epoxy for a gauge length of 2.5 cm. between support points. After mounting the frames in the grips of a tensile testing machine, the sides of the frames were cut. The filaments were then pulled using the 10 or 20 g scale of a 500 g load cell at a crosshead speed of 0.5 cm/minute. Modulus was determined from the linear portion of the stress-strain curve. Diameters were measured for each filament under test to the nearest 0.25 μm . Since diameters varied within the gauge length by $\pm 0.5 \mu m$, the average diameter of each group of filaments was used in the modulus calculation. The results are presented in Table V. The data shows a significant amount of scatter with a coefficient of variation of between 10 and 20% for most data sets. The results indicate that there is no demonstrable effect on the mechanical properties of the filament from either the coating or oxidation procedures.

B. Electrical Properties

During processing of the filaments, resistance measurements were made on the yarns as described in Section II. Variations along the length of the yarn were noted. Typical ranges for as-received, SiC-coated, and oxidized fibers were 5-7, 20-30, and 30-70 ohms respectively.

One sample of yarn which had been oxidized under different conditions (free-floating in the phosphoric acid rather than wound on a spool) gave values in the range from 30-300 ohms.

Individual filament properties were also measured using the apparatus described in Section V. Two types of measurements were performed. In one case, the resistance between the mercury electrodes was measured with an ohm-meter (using a 0.2 or 2 volt measuring potential depending on the scale used). In several cases, the current-voltage curve was measured.

Some variation along the length of individual filaments was noted, but the variations generally were not as severe as on the yarns. Table VI lists individual filament resistance values measured on various samples using an ohm-meter. Most variation was seen in the oxidized sample; hence the range of values along individual filaments is indicated. The oxidized filaments are from oxidation batch #4.

One sample of oxidized filament was of particular interest. It showed a resistance of greater than 20 megohms with an ohm-meter. The current-voltage response was determined for this sample. It exhibited a breakdown voltage of 17.2 volts, below which current was less than 1 microamp. After the initial breakdown, measured resistance was 4.9 K ohms.

One interpretation of the data presented in Table V is that the SiC coating procedure affects all of the filaments in the yarn and increases the resistance by about 1000 ohms as measured here. Further, it would appear that the batch oxidation procedure, although increasing the average resistance further by about 1000 ohms, leaves many filaments unaffected.

Results from a sample of yarn which had been oxidized by suspending a single length of the yarn in the oxidizing solution indicate that an improved procedure would lead to greatly increased resistances. This particular sample provided many individual filaments with resistances in the range from 50-200 K ohms, measured in the same way.

Some care must be exercised in interpreting the resistance data. Figure 21 shows the current-voltage curves determined for two oxidized SiC-coated filaments. Both samples show non-linear I-V behavior. The sample which shows a zero impedance at 0.5 volts was adjacent to an area on the filament which gave a resistance of 72.2 K ohms when measured with an ohm-meter. For the other sample, the resistance measured nearby was 132.8 K ohms; in this case the characterization becomes inaccurate only at voltages greater than about 12 volts.

Breakdown voltages, i.e., that voltage at which current is first perceptible, were generally in the range indicated by Figure 21, from several tenths of a volt up to 2 volts. The exception is the sample noted earlier which exhibited a 17 volt stand-off capability.

VII. Concluding Remarks

The object of this study was to coat T-300 graphite fibers with carbide coatings to increase their electrical resistance. Two pounds of fibers were to be coated with silicon carbide; one pound of this material was to be oxidized to further increase the resistance. Also two pounds of graphite were to be coated with boron carbide.

The study succeeded in establishing deposition conditions in a chemical vapor deposition reactor in which the filament was resistively heated which

- a) deposited a Sic coating in the thickness range of several tenths of a μm ; and
- b) did not substantially alter the mechanical properties of the graphite filaments. Sic-coated filaments could be oxidized in boiling 85% phosphoric acid without detriment to the mechanical properties.

Precise measurement of coating thickness was difficult. Hence, optimum coating conditions could not be specified based on achieving the target thickness of 0.1 μm . Rather optimum conditions were chosen based on maximum strength retention and increase in yarn resistance, consistent with the ability to observe a coating in the thickness range of several tenths of μm or less. If the coatings in fact are thicker than 0.1 μm , the filament density would be increased, but the changes would be relatively small. A 0.1 μm coating would increase density by approximately 2% while a 0.3 μm thick SiC layer would increase the density by less than 6%.

Resistance and current-voltage measurements were made in an apparatus in which electrical contact with single filaments was made through a pair of 1 cm. mercury pools separated by .5 cm. These measurements indicate:

- a) The SiC coating permeates the yarn in that most of the filaments examined showed an increased resistance relative to as-received filaments.
- b) The increase in resistance due to SiC coating was approximately 1000 ohms.
- c) Filaments batch oxidized on a spool in boiling phosphoric acid showed varied results, indicating variation in the degree of oxidation.
- d) Batch oxidized filaments showed increases in average resistance of 1000 ohms, with values as high as 8000 ohms.

Samples of filament oxidized by suspending a single strand of yarn in the oxidizing medium showed greater increases in resistance, up to approximately 160 K ohms.

Measurements of the current-voltage curves on the above filaments and on other samples of SiC and B_4C coatings applied to carbon monofilament show that the coated filaments exhibit non-linear current-voltage curves including examples of negative and zero impedance. Electrical measurements on B_4C coated carbon monofilament indicate that thin layers of B_4C would be ineffective in increasing filament resistance.

The study shows that oxidized SiC-coated graphite filaments have exhibited high electrical resistance and high stand-off voltages (up to 17 volts) with no decrease in mechanical properties. Further work remains to be done to develop a practical oxidation apparatus to completely and uniformly oxidize the SiC coatings.

It was not technically feasible within the scope of this contract nor advisable, given the results of the electrical measurements, to develop a deposition process for coating graphite filaments with B_4C .

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3. "Phosphoric Acid and Fused Salt Etching of Silicon Carbide", R. C. Ellis, Jr., *ibid*, page 420
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TABLE I - EFFECTS OF PROPANE ADDITION ON COATED YARN PROPERTIES

Run Number	Residence Time (Sec)	Coating Temperature K	Propane Flow 1/min.	Resistance Ohms	% Strength Retention
20	6	1120°	0.1	----	93
27			0.1	15 - 25	99
22			0	17 - 18	92
25			0	8 - 12	85
16	4.5	1090°	0.1	15 - 22	119
		1120°	0.1	11 - 24	112
			0	25 - 30	106
			0	10 - 16	91

TABLE II - EFFECTS ON YARNS OF THE ADDITION OF AN O₂, N₂ MIXTURE TO THE PLATING GAS

Run Number	Residence Time (sec)	Coating Temperature K	Propane Flow l/min.	O ₂ , N ₂ Flow l/min.	Resistance Ohms	% Strength Retention
34	4.5	1120°	0	0	10-16	91
35			0.1	0	11-24	112
36			0.1	0.04	15-40	97
37			0	0.04	9-18	95

LII

TABLE III - EFFECTS OF VARIATIONS IN HYDROGEN TO SILANE
RATIO ON COATED YARN PROPERTIES

Run Number	Hydrogen l/min.	Silanes l/min.	Argon l/min.	Hydrogen/Silane	Deposition Temperature, K	Residence Time, Sec.	Resistance ohms	% Strength Retention
Optimum	0.425	0.8	0	0.53	1080 - 1120	4.5	20 - 30	100
43	0.425	0.6	0.14	0.71	1170	4.5	-	33
44	0.425	1.2	0	0.35	1170	7.5	17 - 19	44
45	0.48	0.4	0	1.2	1110	6.4	32 - 50	38
47	0.48	0.4	0.175	1.2	1110	9	-	48
61	0.6	0.8	0.21	0.75	1325	5.5	30 - 70	32
62	0.6	0.8	0.35	0.75	1170	5.5	30	30

TABLE IV - STRENGTH RETENTION AND WEIGHT LOSS OF SiC-COATED T-300 YARNS
VS. COATING AND OXIDATION CONDITIONS*

Coating Run	Oxidation Temperature K	Time Minutes	Resistance Change, %	% Weight Loss	% Strength Retention
30	1073°	5	0	6.6	77
30		10	0	9.1	54
31		10	-50	12.1	56
32		10	0	6.5	58
33		10	0	8.7	56
30	1173°	10	+100	37	36
35		15	+50	29	29
36		25	+30	32	39
30**	1273°	10	+150	29	36
31		15	+250	67	4
33		10	+60	57	6

*In an atmosphere of argon and 100 torr H₂O

**Comparison with other data suggests temperature was lower than 1273K

TABLE V - MECHANICAL PROPERTIES OF COATED GRAPHITE FILAMENTS

Fiber	As Received T-300	SiC Coated	SiC-Coated Oxidized
Average Breaking Load, Grams	8.8	8.4	10.2
High	11.6	9.5	13.1
Low	6.0	5.8	7.8
Std. Deviation	1.8	1.1	1.5
No. of Tests	10	10	10
<hr/>			
Modulus GPa (Msi)	193 (28.0)	186 (26.9)	183 (26.5)
High	210 (30.4)	230 (33.3)	214 (31.0)
Low	161 (23.3)	148 (21.5)	152 (22.0)
Std. Deviation	19 (2.7)	26 (3.7)	19 (2.7)
No. of Tests	10	10	9

TABLE VI - RESISTANCES OF COATED SINGLE FILAMENTS
LENGTH BETWEEN ELECTRODES IS 5 mm

Fiber Type Sample # \	As Received T-300	SiC-Coated	SiC-Coated, Oxidized
1	3.06 KΩ	1.98 KΩ	2.2 - 3.6 KΩ
2	1.95	2.18	2.4 - 3.4
3	2.3	3.45	3.0 - 2.7
4	2.0	3.20	2.5 - 3.7
5	1.88	2.95	8.4 - 10.0
6	1.70	2.25	2.6 - 3.0
7	1.77	2.30	2.2
8	1.80	3.25	2.0 - 2.9
9	1.87	3.34	3.0 - 5.4
10	1.88	2.35	3.4 - 3.5
11	1.77	3.17	3.5 - 3.6
12	1.78	3.41	2.6 - 3.6
13	1.80	1.95	3.7 - 4.0
14	1.77	3.40	5.4 - 5.5
15	1.89	2.48	2.9 - 3.1
16	1.84	2.40	>20 MΩ
17	1.86	3.50	
18		3.37	
Average	1.94KΩ	2.83KΩ	3.67KΩ
Std. Deviation	.32	.57	1.7

*Average based on the mean of the range

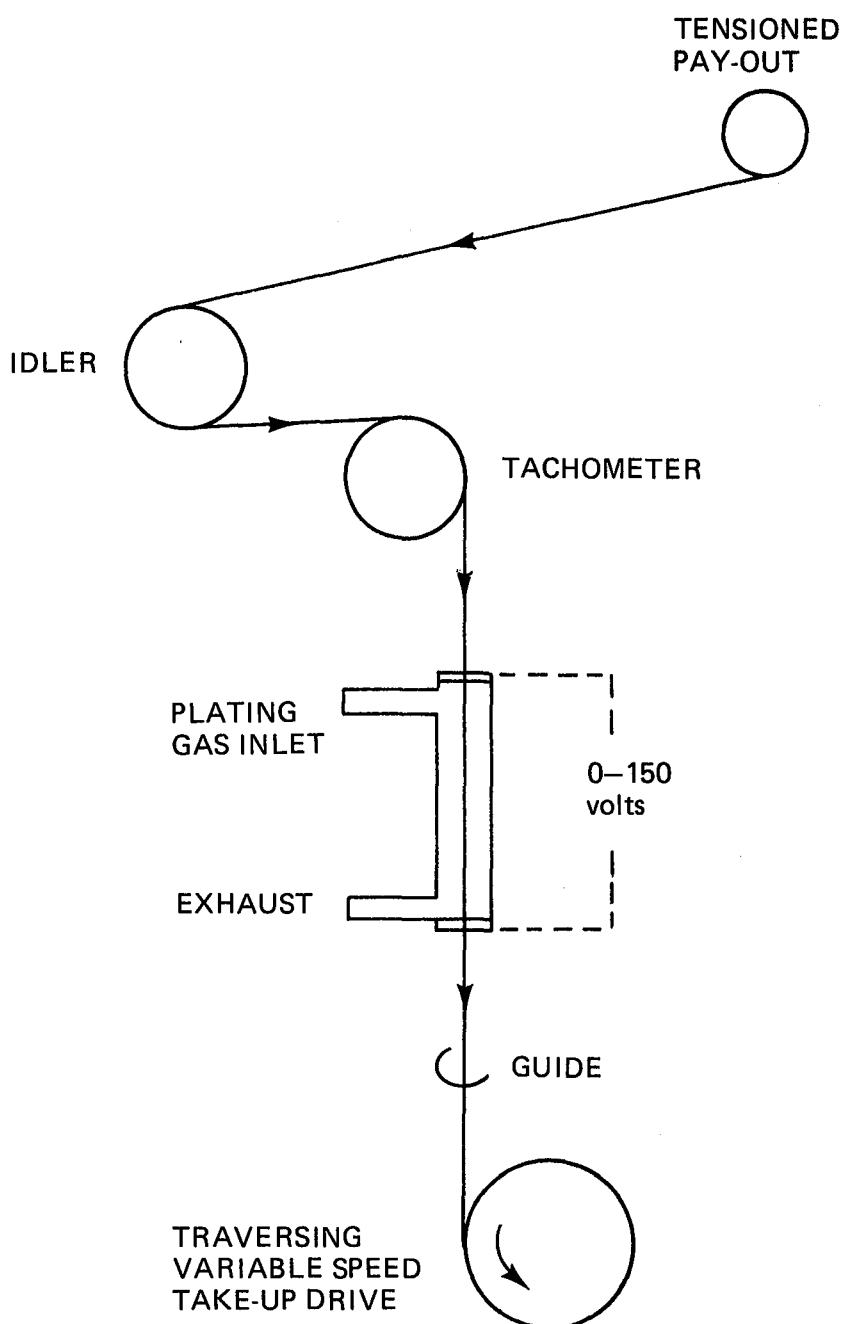


Figure 1. VERTICAL CHEMICAL VAPOR DEPOSITION REACTOR

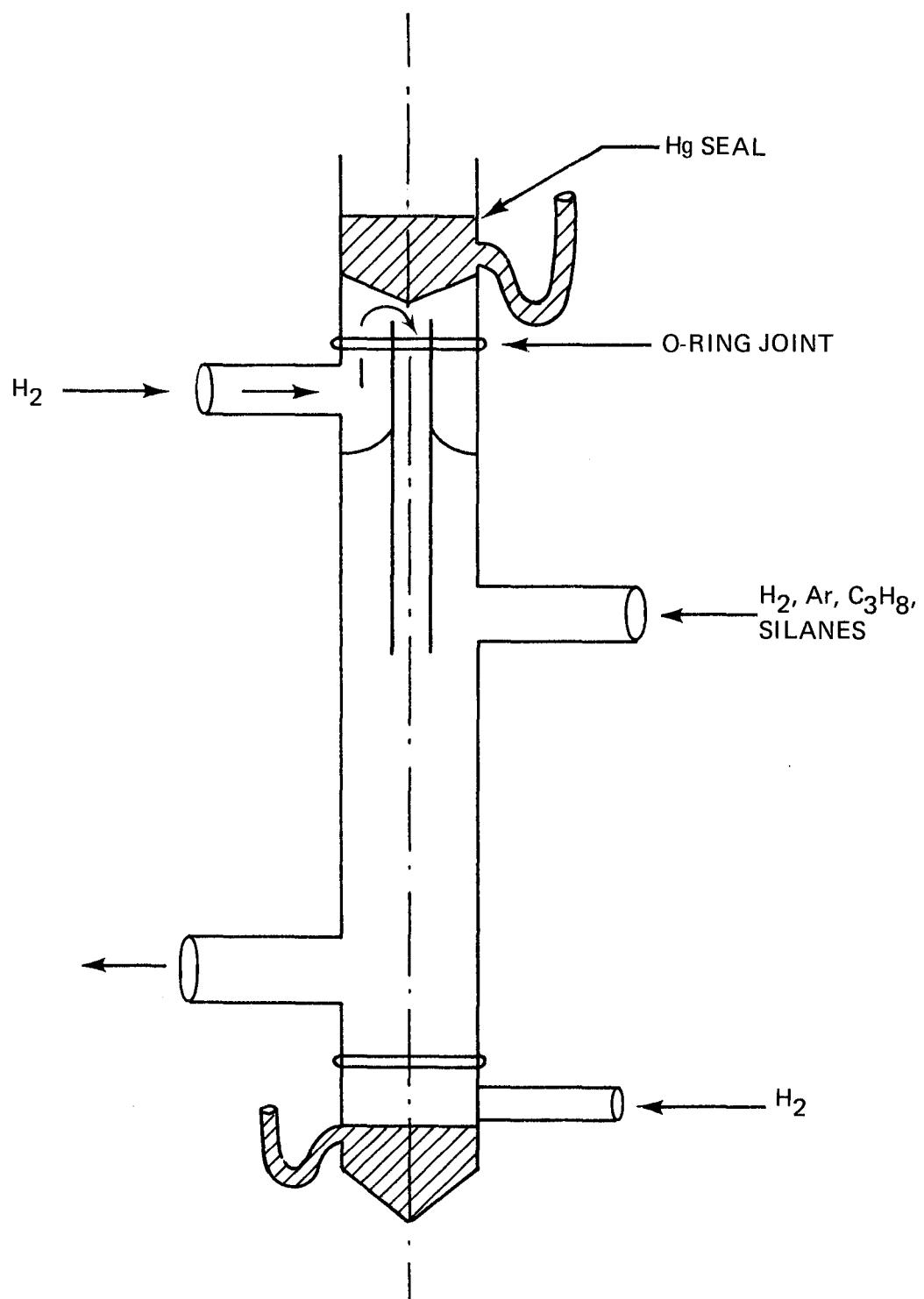


Figure 2. REACTOR TO COAT GRAPHITE WITH SiC; SCALE: APPROXIMATELY 1:1

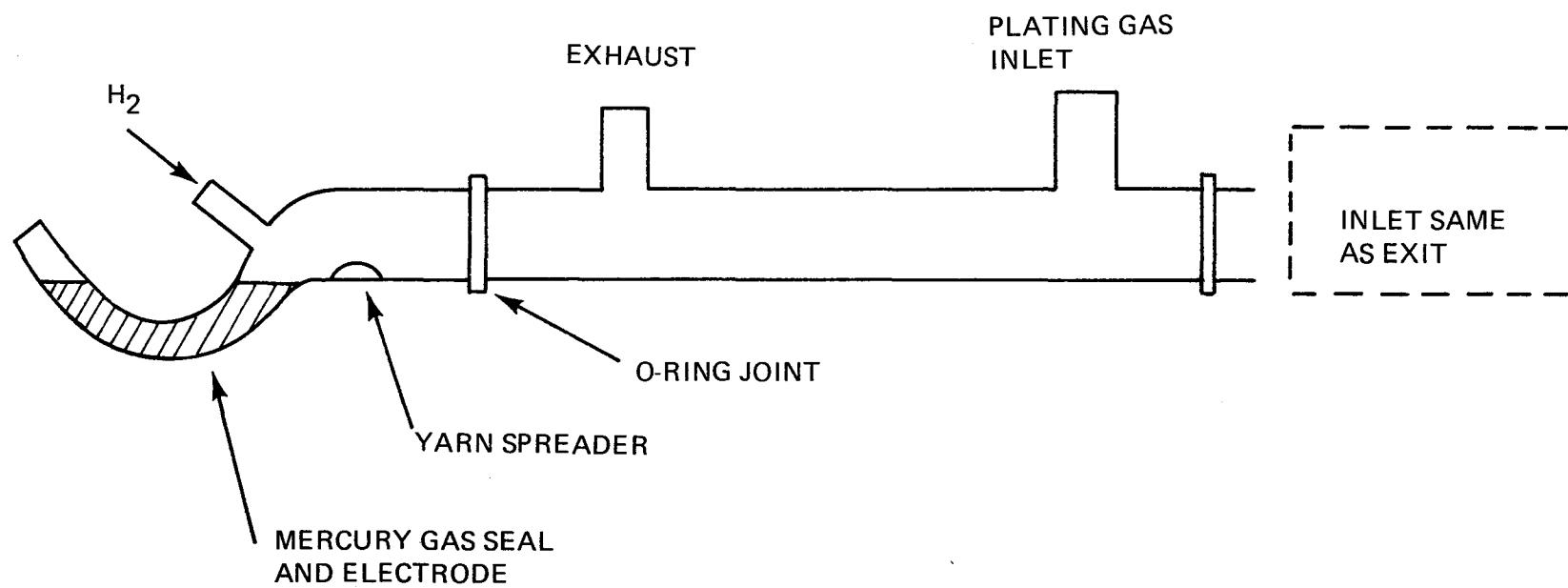


Figure 3. HORIZONTAL CVD REACTOR

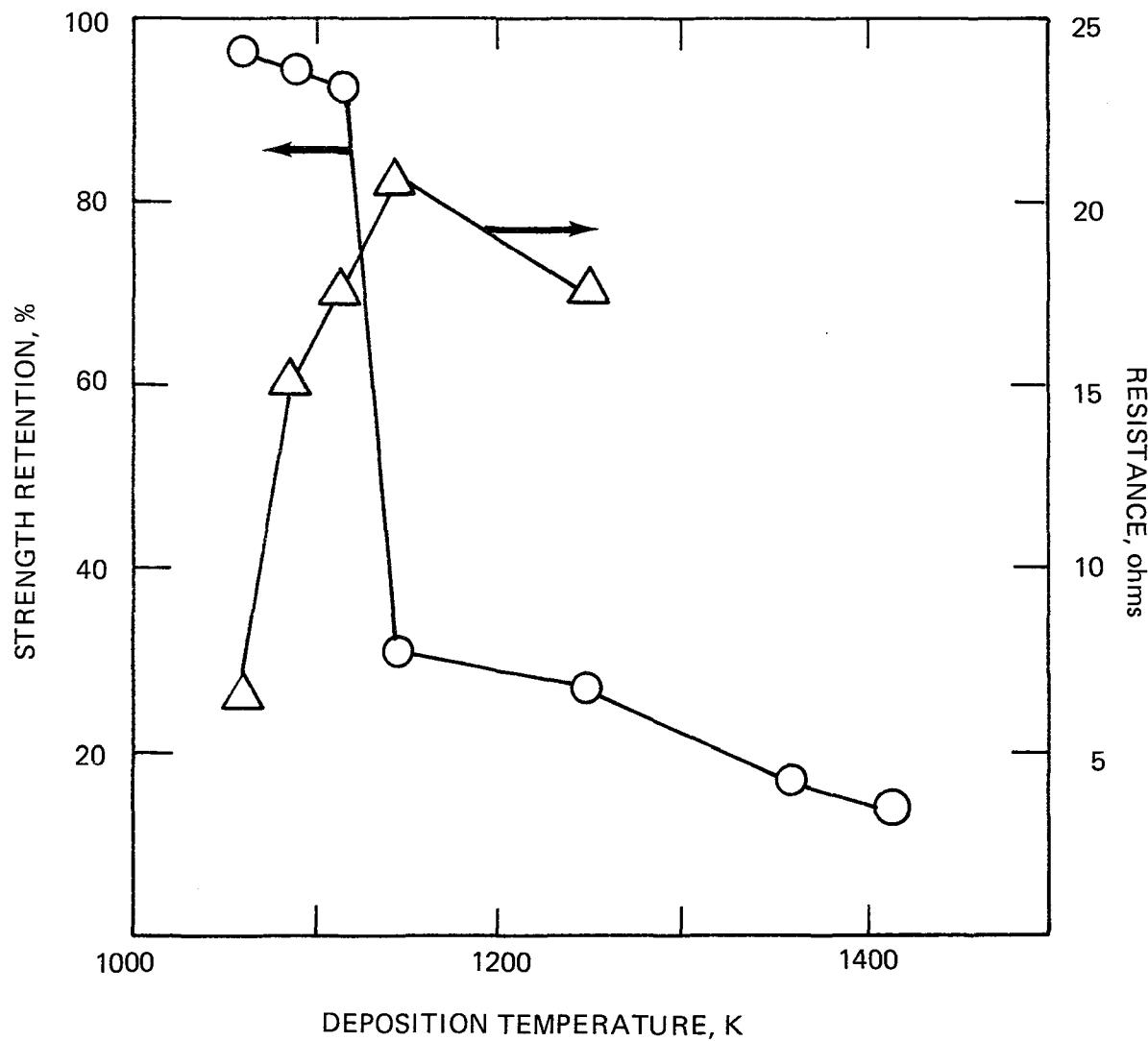


Figure 4. STRENGTH AND RESISTANCE OF YARNS VS. DEPOSITION TEMPERATURE; FIVE SECOND RESIDENCE TIME

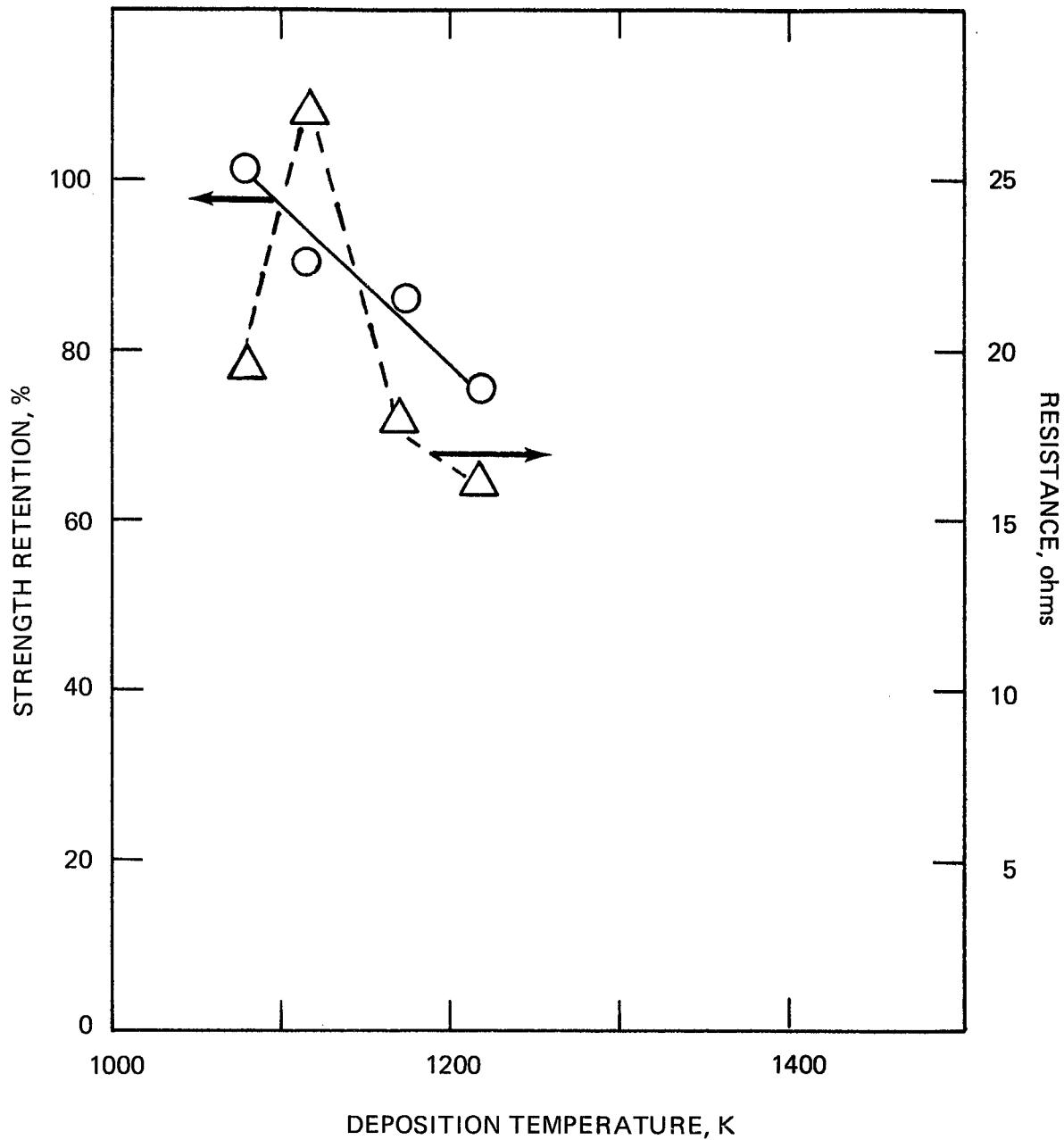


Figure 5. STRENGTH AND RESISTANCE OF YARNS VS. DEPOSITION TEMPERATURE; 4.5 SECOND RESIDENCE TIME

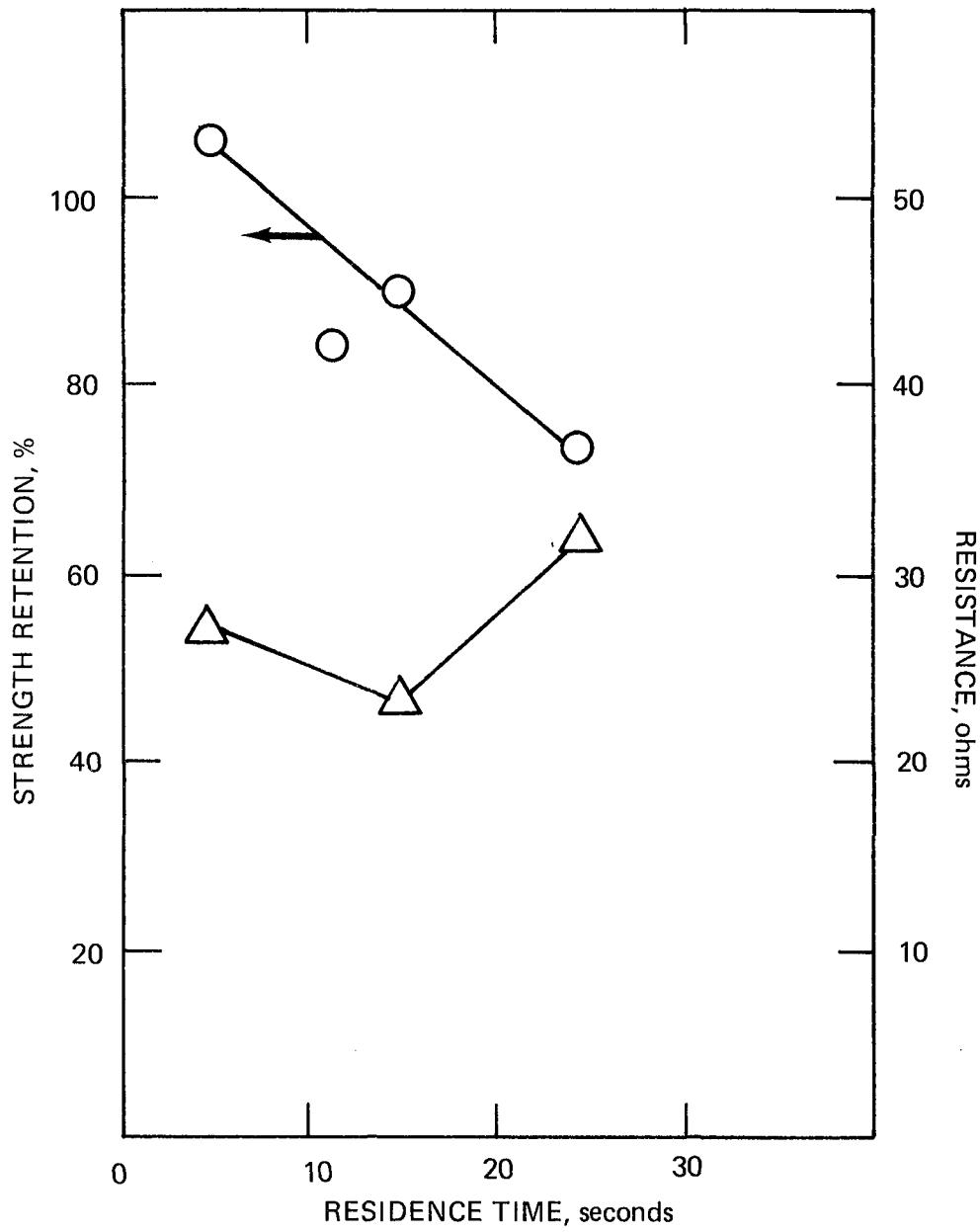


Figure 6. STRENGTH AND RESISTANCE OF YARNS VS. RESIDENCE TIME
T = 1120 K

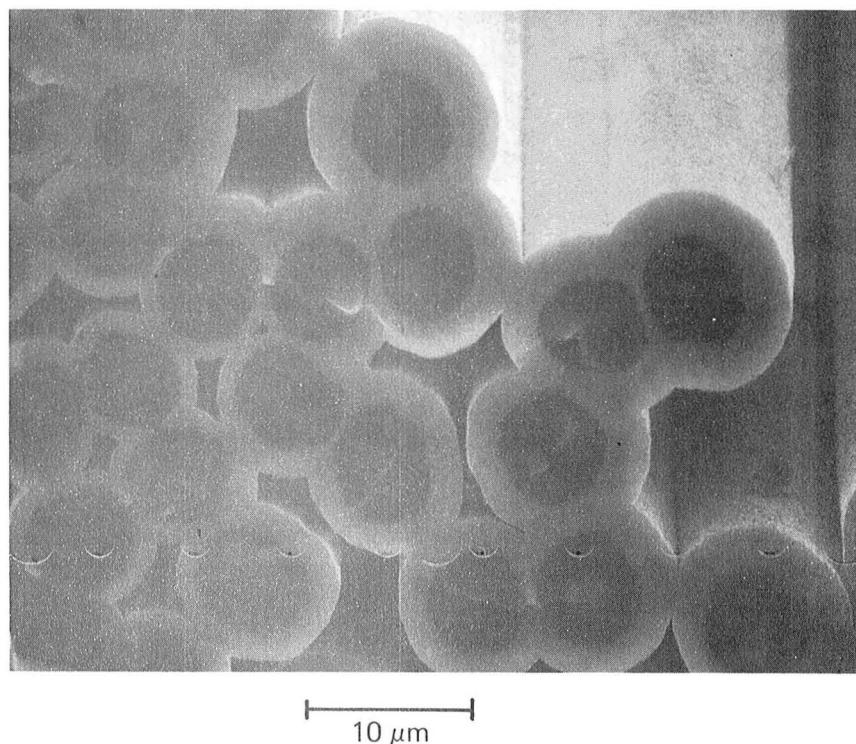
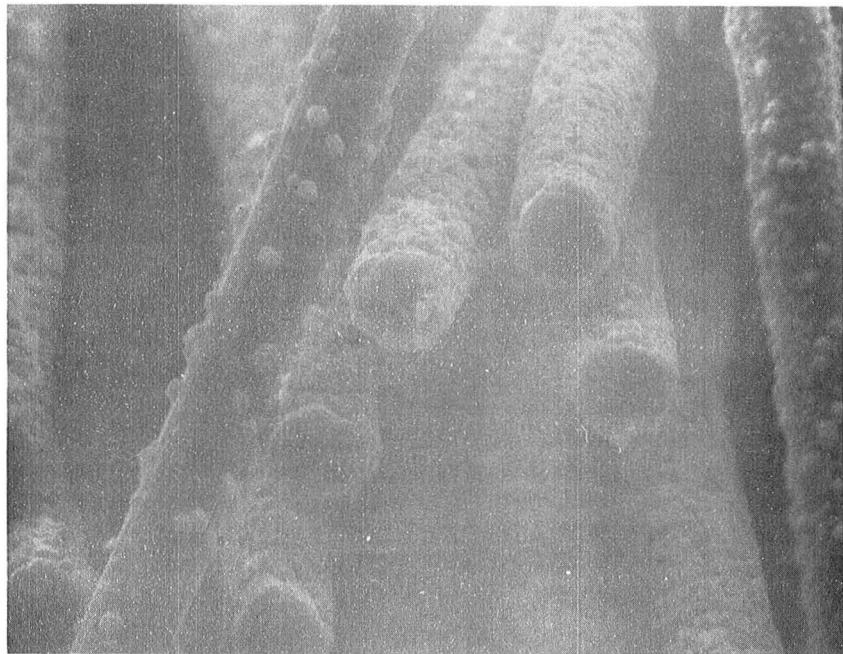


Figure 7. SEM OF THICK SiC COATING



a. $T = 1400$ K

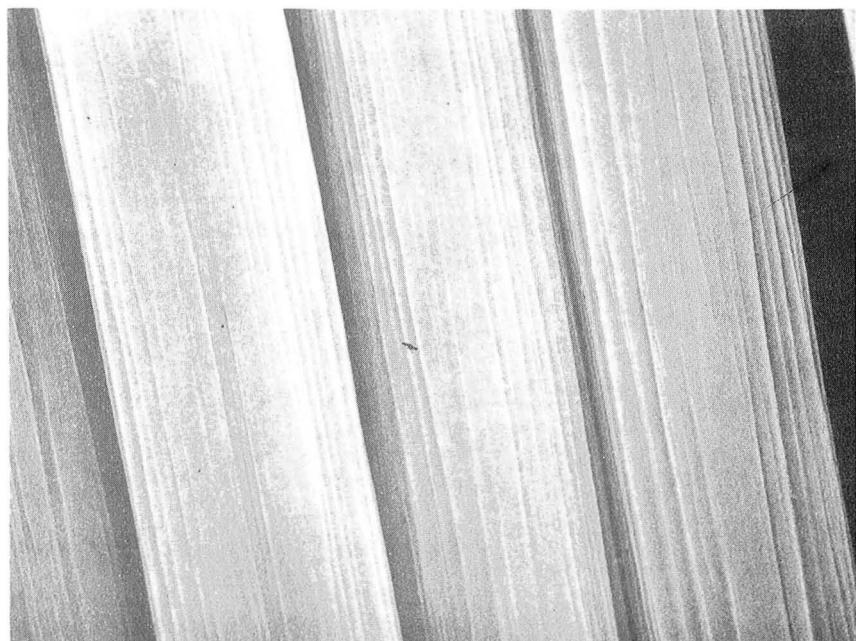
10 μ



b. $T = 1170$ K

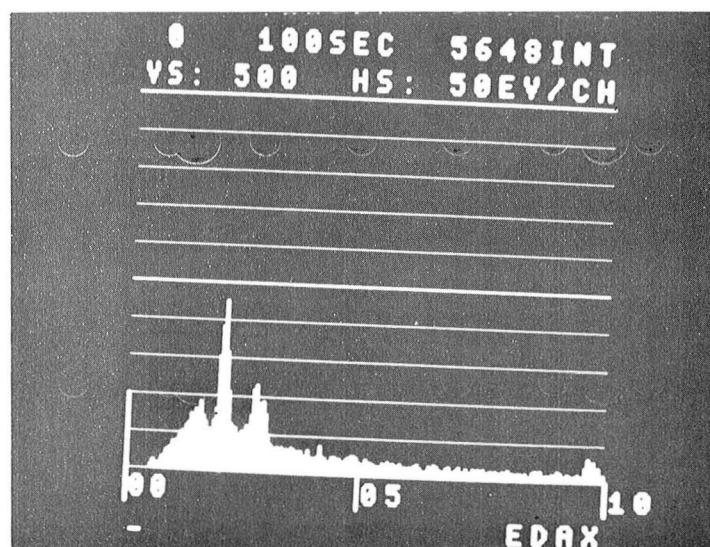
1 μ

Figure 8. SEM PHOTOMICROGRAPHS OF SiC COATINGS
PRODUCED AT VARIOUS TEMPERATURES



c. $T = 1080^\circ K$

1μ



d. EDAX OF
FIBER c. ABOVE

Si-Au-Pd

Figure 8. CONTINUED

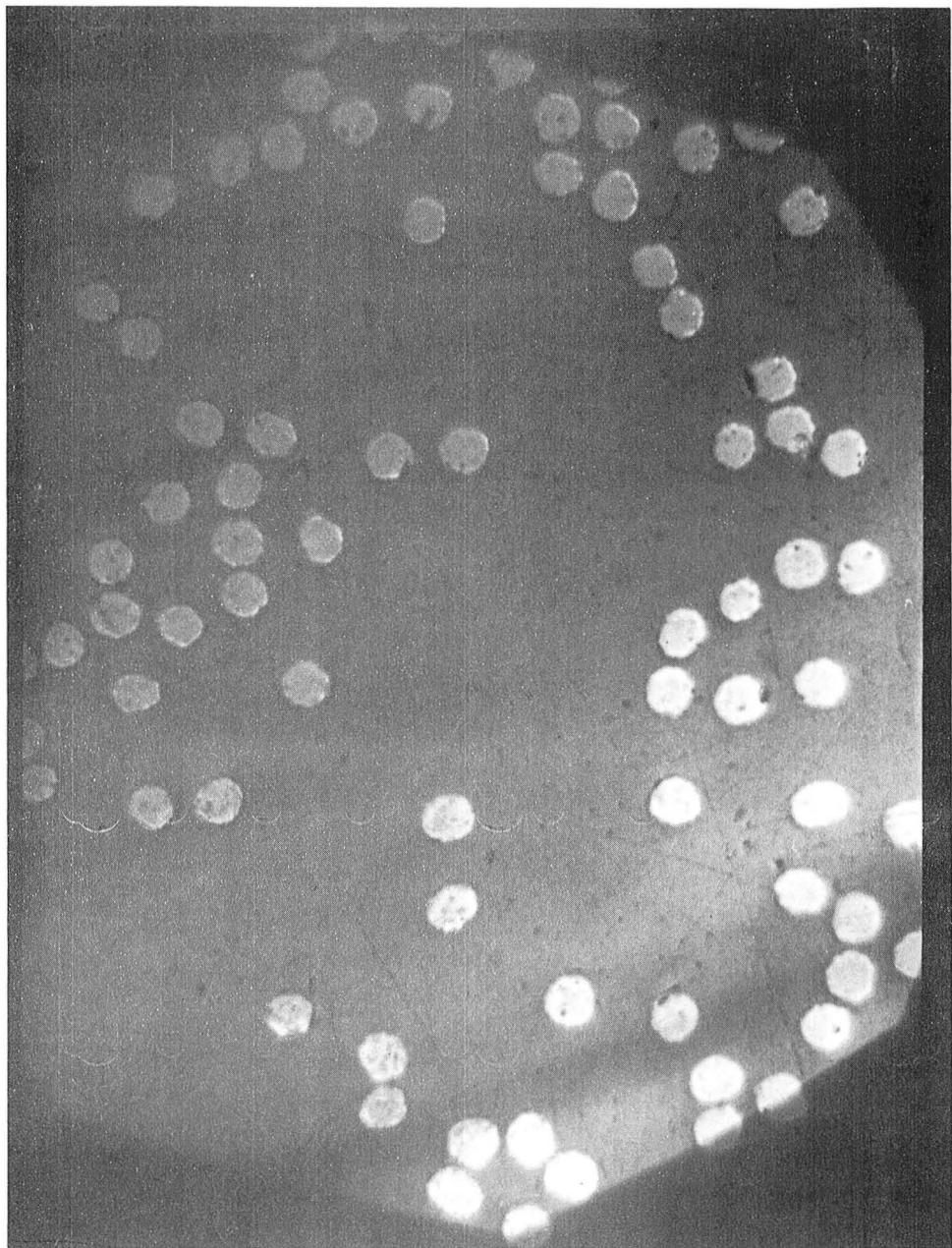


Figure 9. METALLOGRAPH OF OPTIMIZED SiC COATED FIBERS

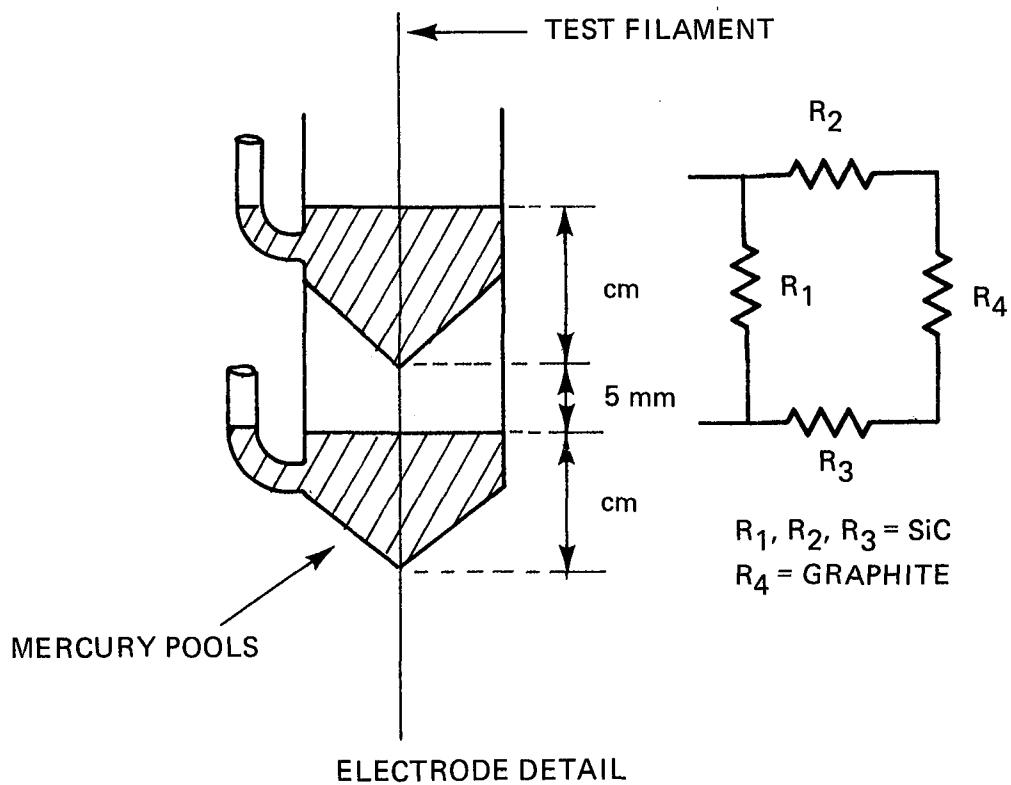
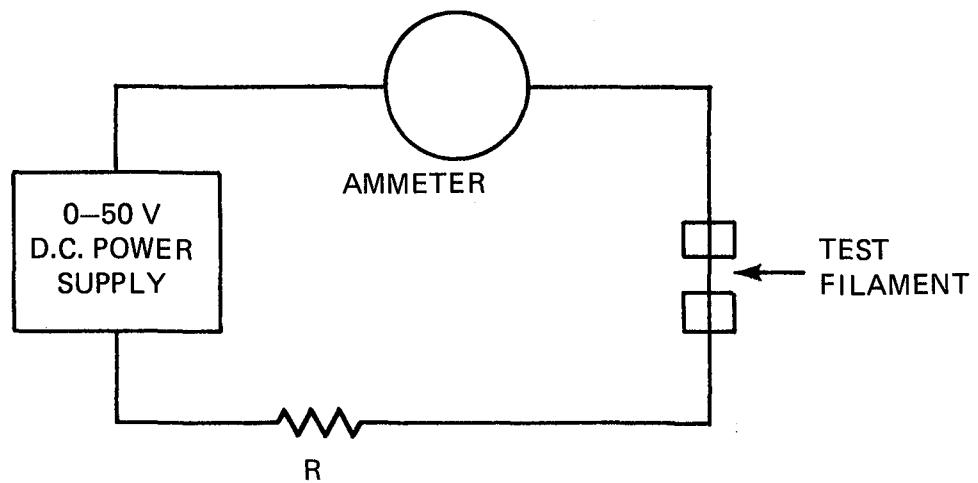


Figure 10. APPARATUS FOR DETERMINATION OF ELECTRICAL PROPERTIES OF CARBIDE COATINGS

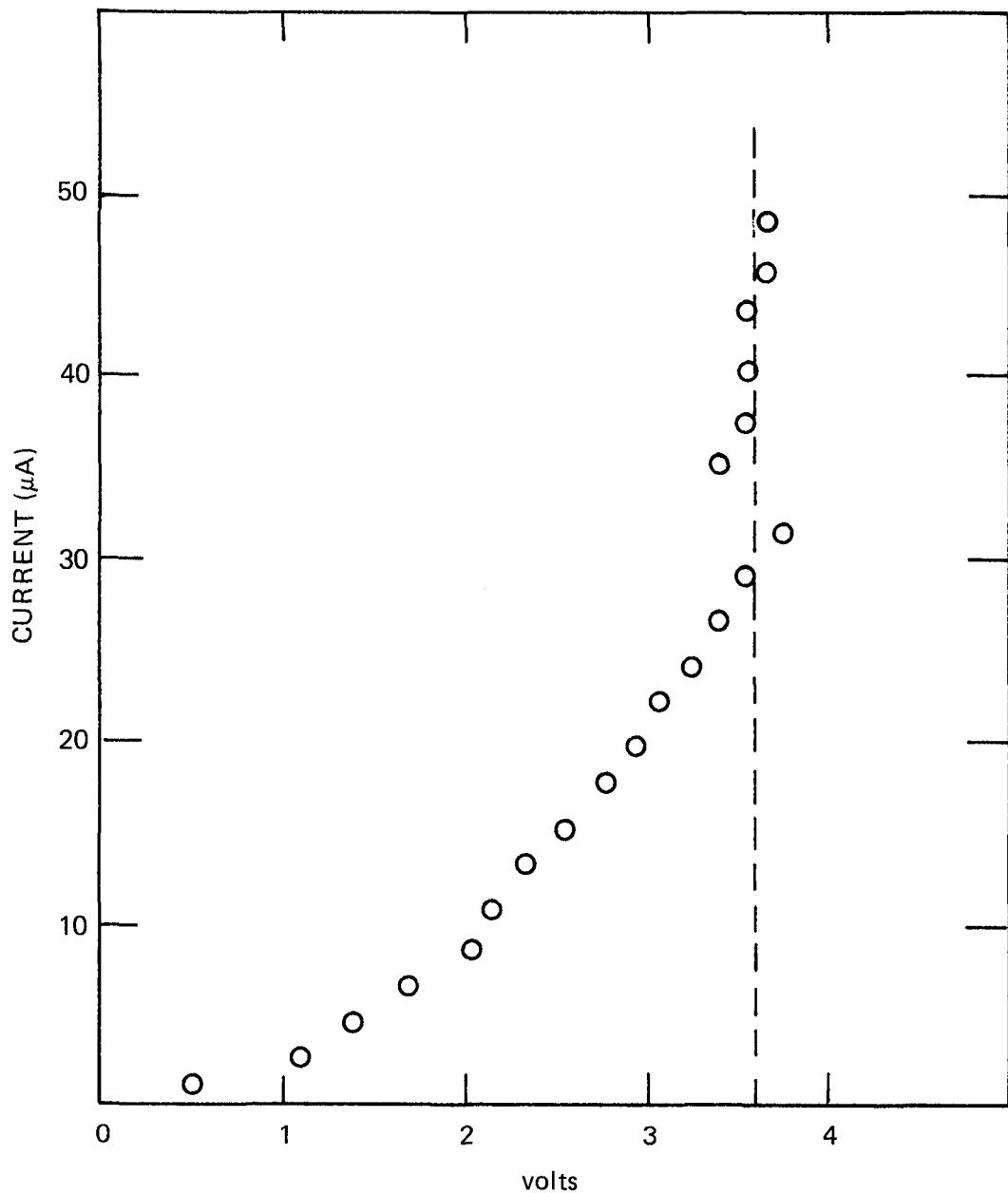


Figure 11. CURRENT VS. VOLTAGE FOR A 29 μ m THICK COATING
OF SiC ON CARBON MONOFILAMENT

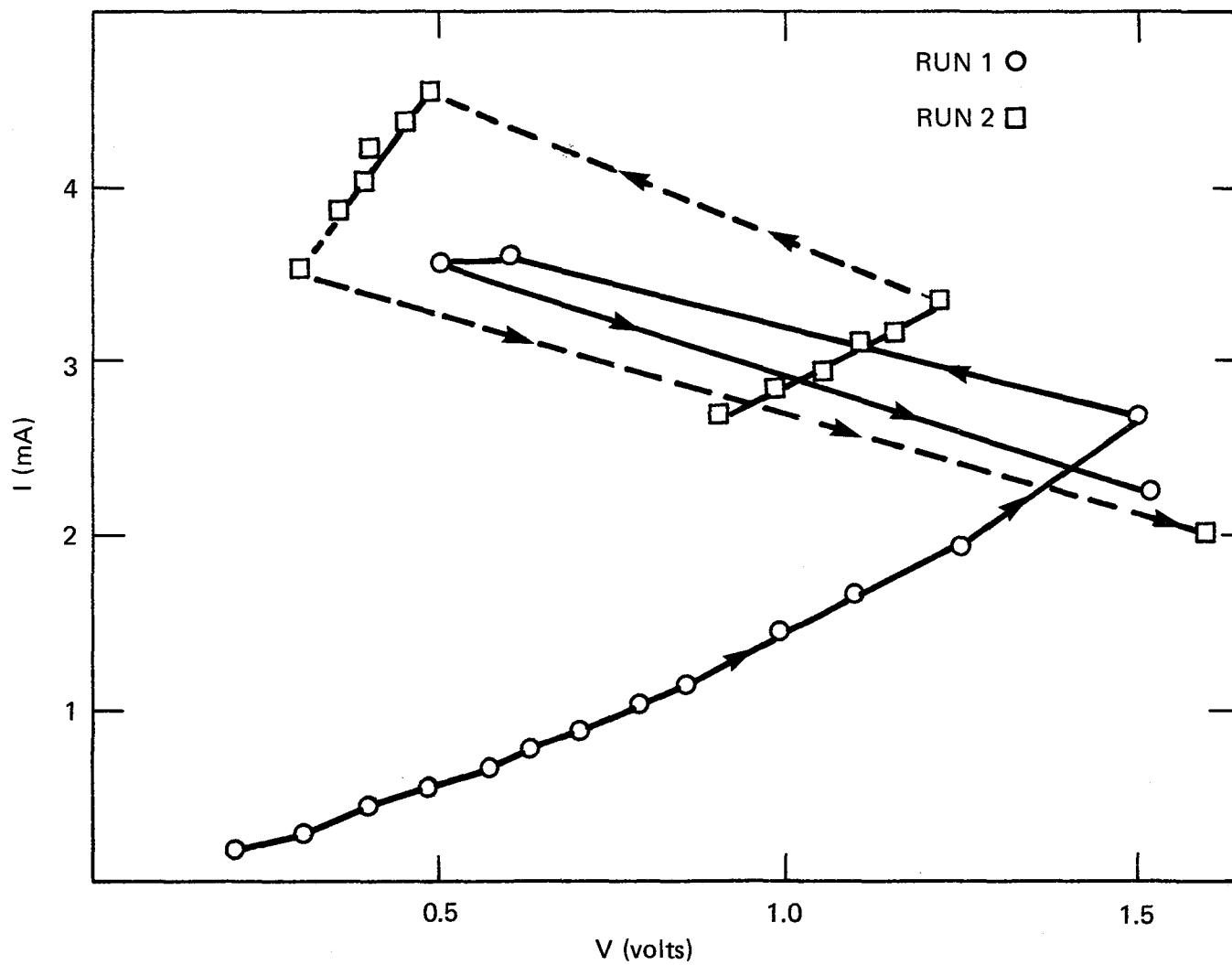


Figure 12. CURRENT-VOLTAGE CHARACTERISTIC OF A THIN SiC COATING ON CARBON MONOFILAMENT

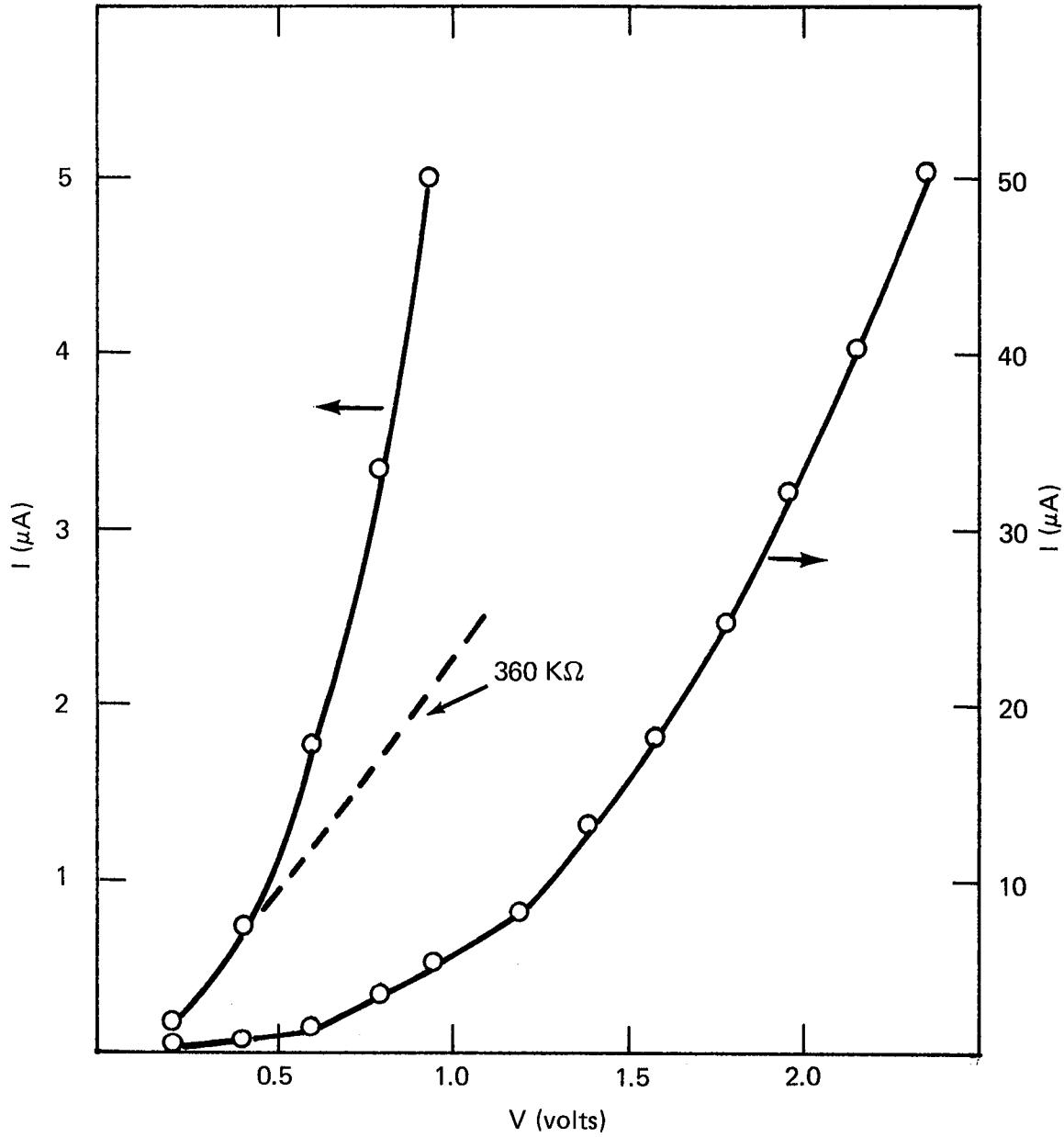


Figure 13. CURRENT-VOLTAGE CHARACTERISTICS OF 3.3-4.2 μm OF SiC
ON CARBON MONOFILAMENT

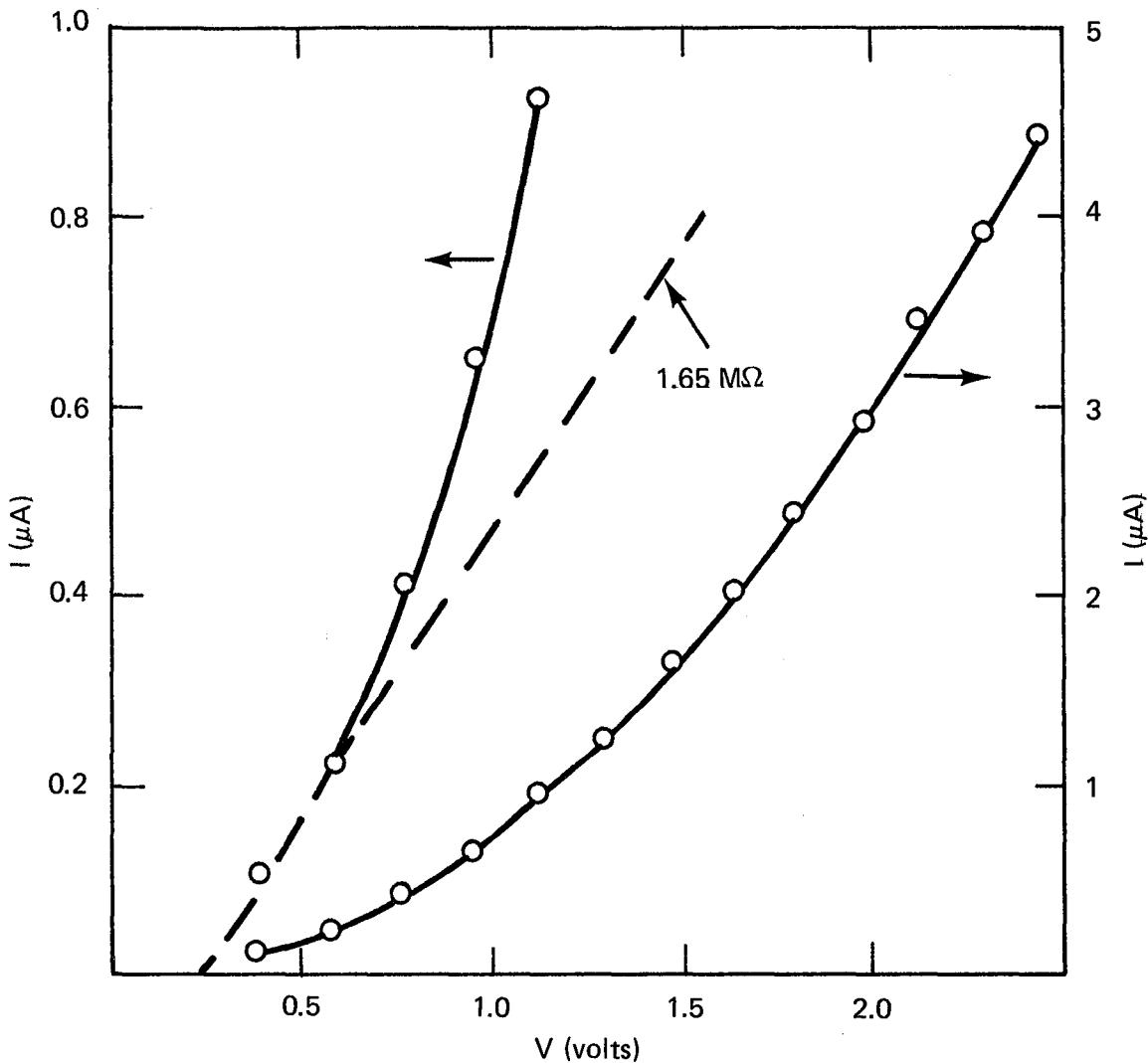


Figure 14. CURRENT-VOLTAGE CHARACTERISTIC OF 8.5-9.0 μm SiC
ON CARBON MONOFILAMENT

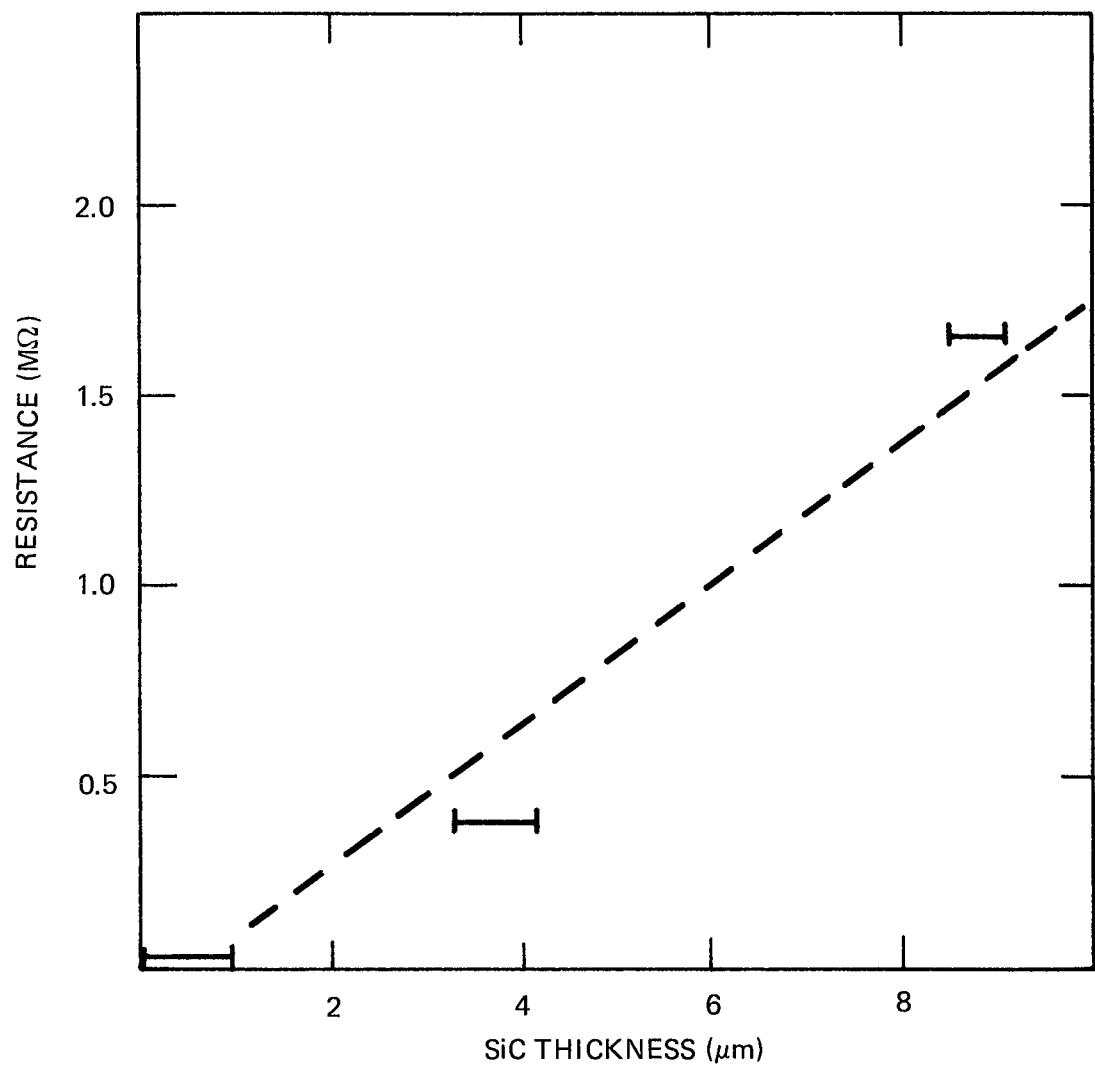


Figure 15. ELECTRICAL RESISTANCE VERSUS SiC COATING THICKNESS

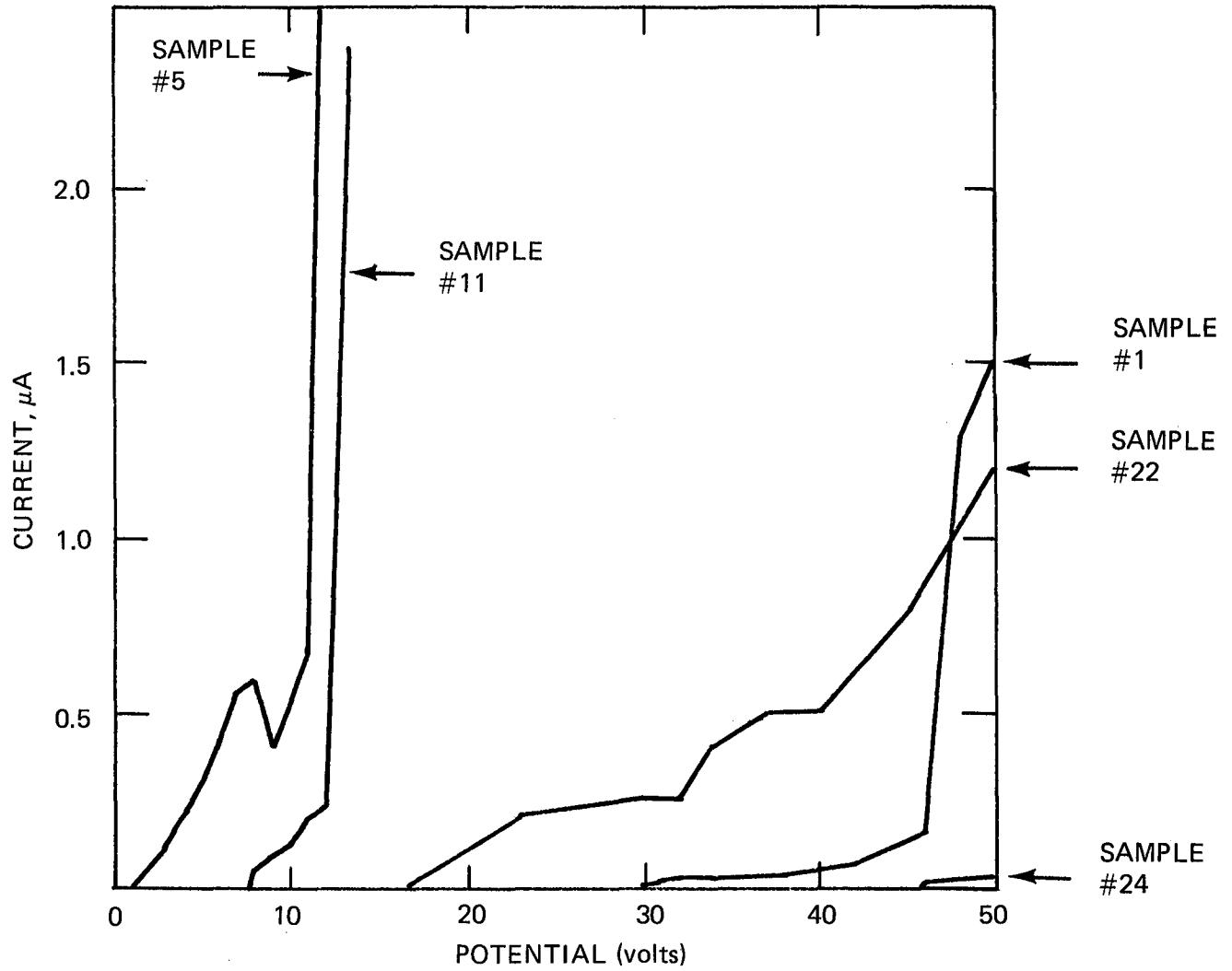


Figure 16. CURRENT VS. VOLTAGE FOR OXIDIZED SiC COATINGS ON CARBON MONOFILAMENT; SiC THICKNESS IS 55 μm

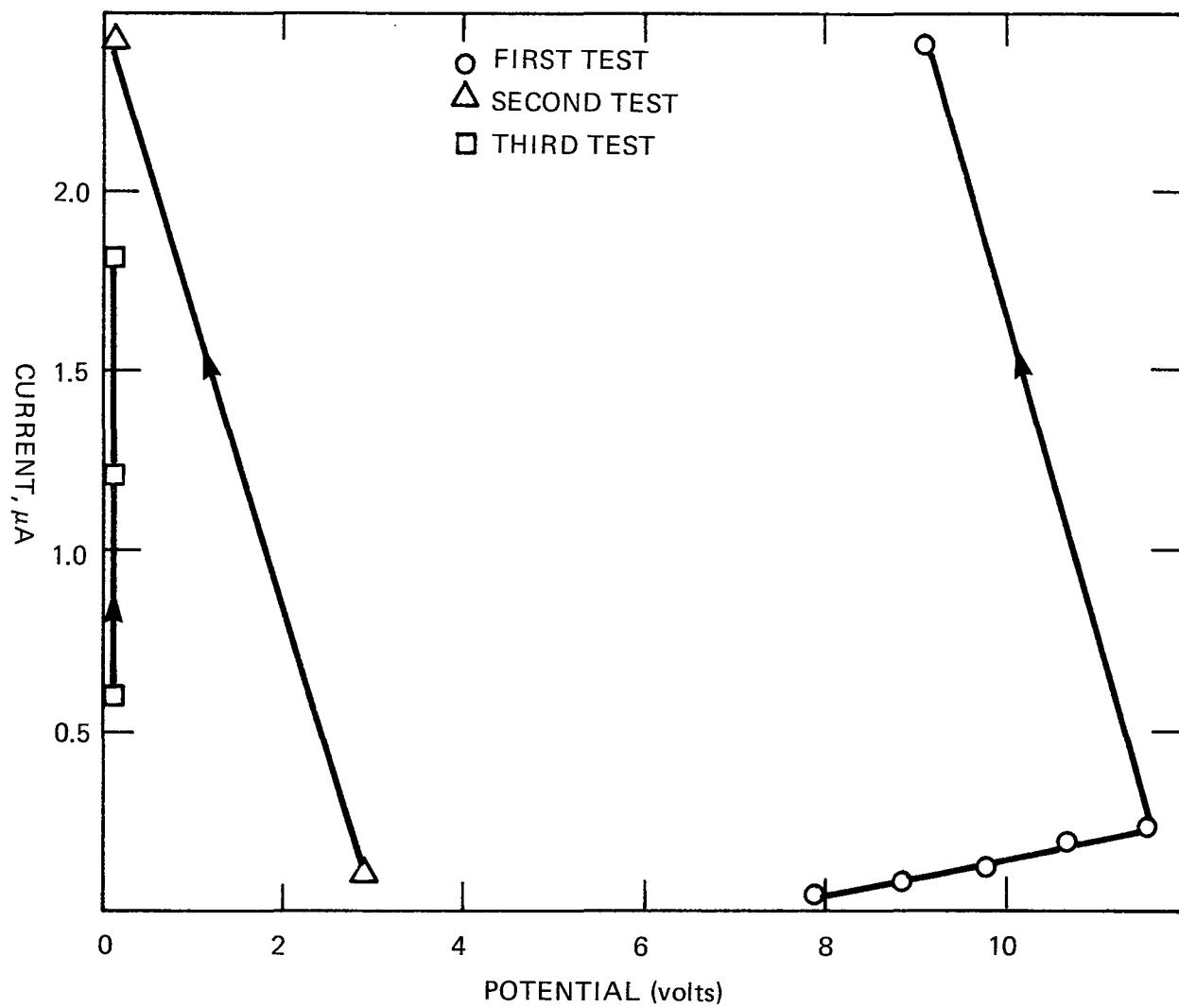


Figure 17. REPEATED TESTS OF BREAKDOWN VOLTAGE ON A SINGLE
OXIDIZED SiC-COATED CARBON MONOFILAMENT SAMPLE

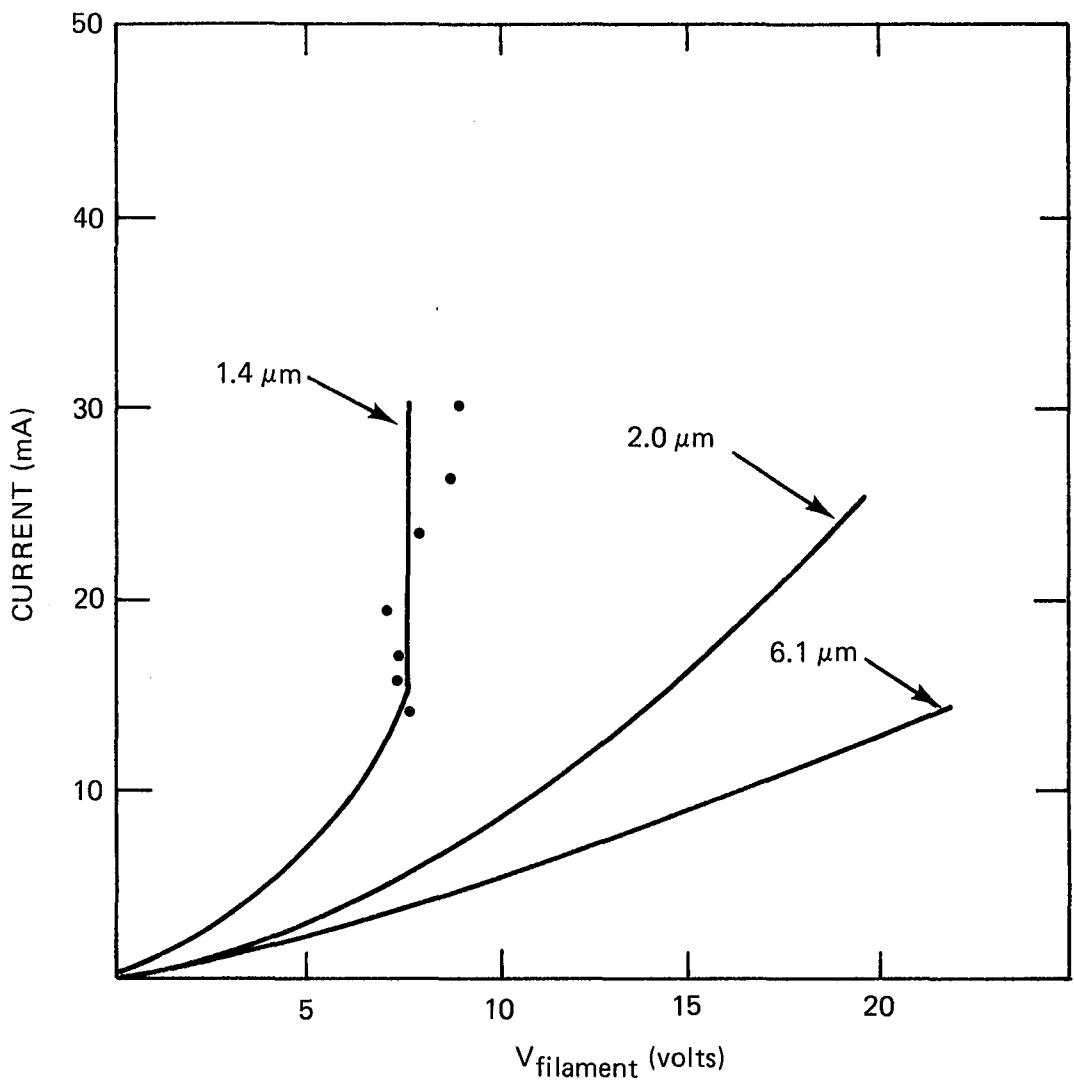


Figure 18. CURRENT-VOLTAGE CHARACTERISTICS FOR B_4C COATINGS
OF VARIOUS THICKNESSES ON CARBON MONOFILAMENT

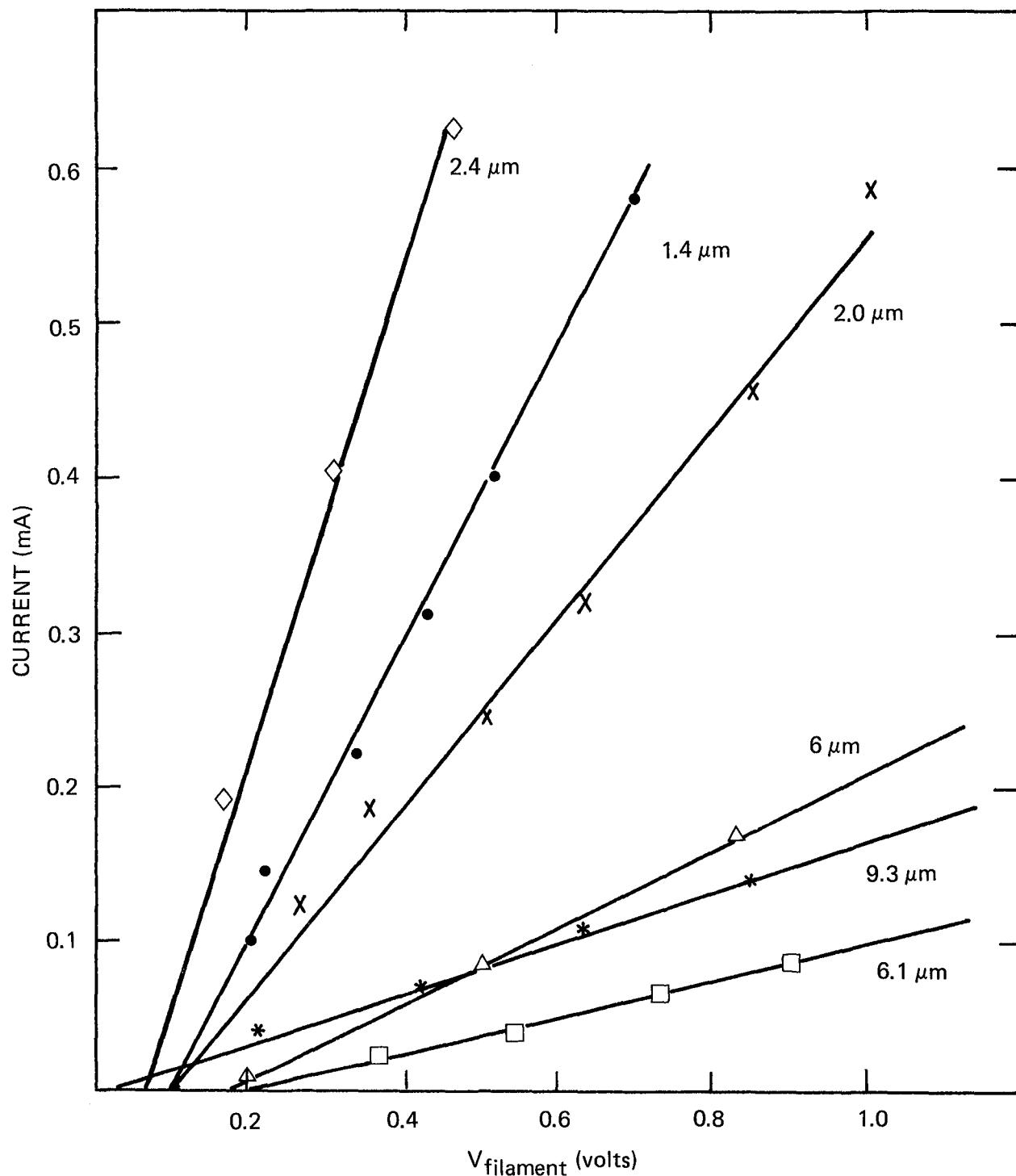


Figure 19 CURRENT-VOLTAGE FOR B_4C COATINGS IN THE LINEAR REGION

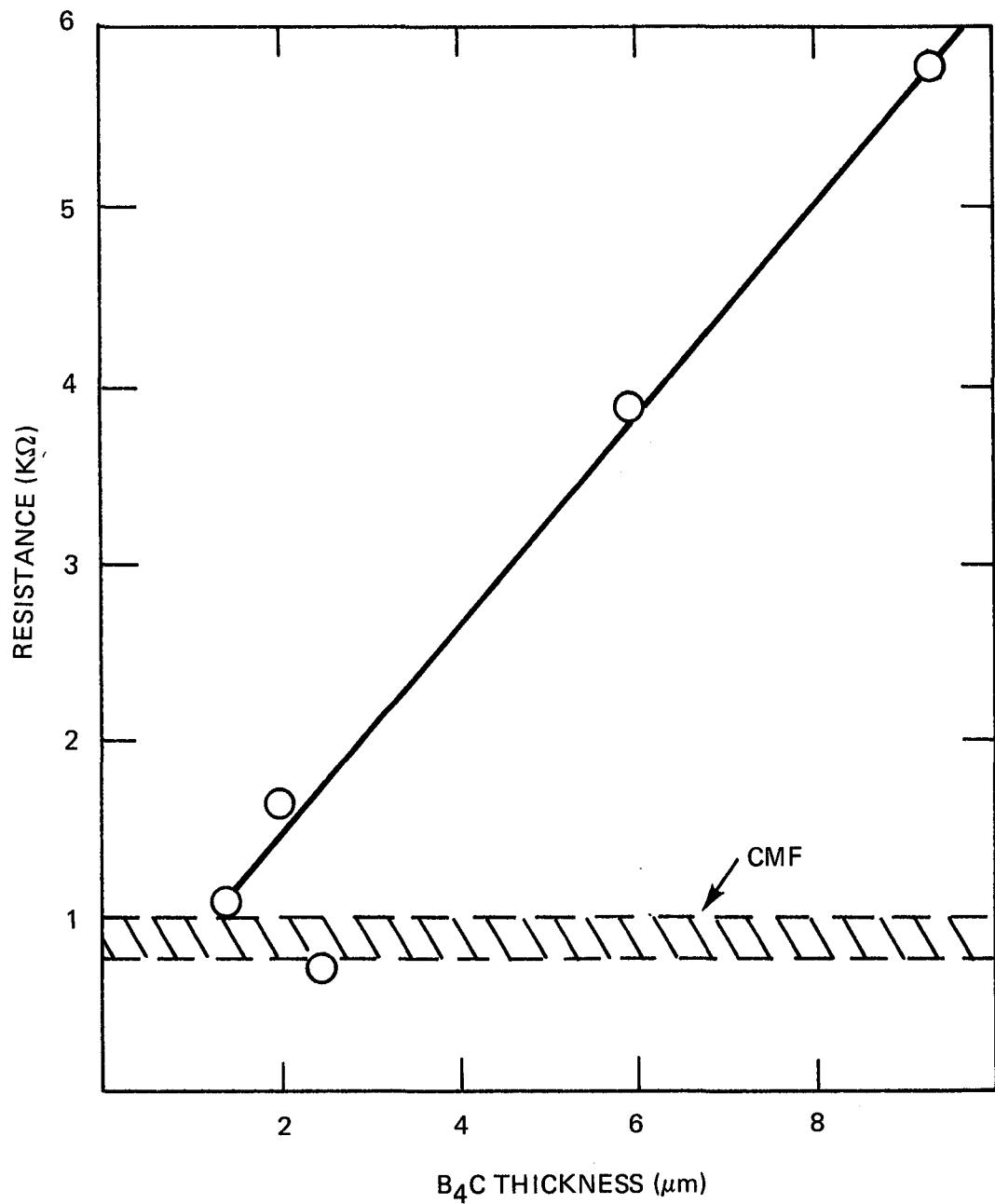


Figure 20. RESISTANCE VS. B_4C COATING THICKNESS

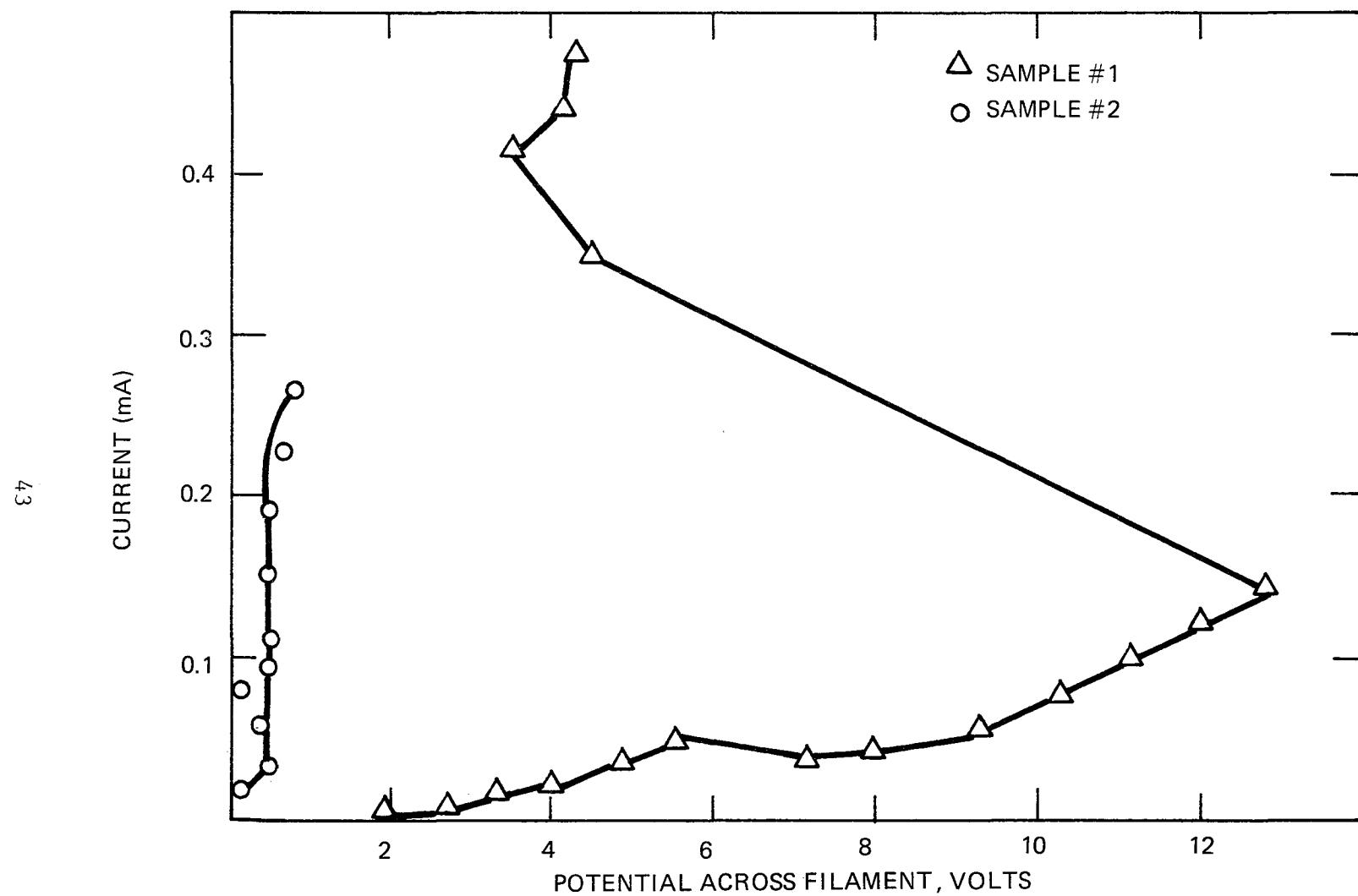


Figure 21. CURRENT-VOLTAGE CURVES FOR OXIDIZED SiC-COATED GRAPHITE FILAMENTS

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4. Title and Subtitle A Study of the Deposition of Carbide Coatings on Graphite Fibers		5. Report Date September 1979	
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		14. Army Project No.	
15. Supplementary Notes Contract Monitor: Dennis Dicus, NASA Langley Research Center			
16. Abstract The chemical vapor deposition of boron carbide and silicon carbide on graphite fibers to increase their electrical resistance was studied. Silicon carbide coatings were applied without degradation of the mechanical properties of the filaments. These coatings typically added 1000 ohms to the resistance of a filament as measured between two mercury pools. When SiC-coated filaments were oxidized by refluxing in boiling phosphoric acid, average resistance increased by an additional 1000 ohms; in addition, resistance increases as high as 150 K ohms and breakdown voltages as high as 17 volts were noted. Data on boron carbide coatings indicated that such coatings would not be effective in increasing resistance, and would degrade the mechanical properties.			
17. Key Words (Suggested by Author(s)) Boron Carbide Coating Silicon Carbide Coating Chemical Vapor Deposition Composites Graphite Fibers		18. Distribution Statement Unclassified - Unlimited	
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